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PROGRESS REPORT
OF THE
**SOUTHERN UTILIZATION RESEARCH
AND DEVELOPMENT DIVISION
MARKETING AND NUTRITION RESEARCH**

JULY 1, 1970

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UNITED STATES DEPARTMENT OF AGRICULTURE

This progress report includes a summary of Division and cooperative research, a preliminary report of progress, and a list of publications for April 1, 1969, through June 30, 1970.

The summaries of progress include some tentative results that have not been tested sufficiently to justify general release. Such findings, when adequately confirmed, will be released promptly through established channels. Therefore, the report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff and others having a special interest in the development of public agricultural research programs.

This report was compiled in the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana 70124.

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PROGRESS REPORT OF THE
SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
MARKETING AND NUTRITION

July 1, 1970

INTRODUCTION

ORGANIZATION OF THE DIVISION

The Southern Utilization Research and Development Division currently conducts research on cotton, cottonseed, peanuts, citrus and subtropical fruit, vegetables, naval stores, sugarcane, sweet sorghum, and rice. The program includes basic and applied research in the physical and biological sciences and in engineering. Basic research plays a key role in uncovering new information that later may be exploited in applied research and development. When appropriate, engineers carry out pilot-plant studies of promising laboratory developments to provide engineering and cost data essential to determining feasibility for industrial application. Division scientists consult with specialists from other organizations during both the planning and the execution of the research, and cooperate actively with industry to facilitate commercialization and utilization of new findings.

The Division's research staff is organized into nine commodity-oriented Laboratories (Cotton Finishes, Cotton Chemical Reactions, Cotton Mechanical, Cotton Physical Properties, Textiles and Clothing, Oilseed Crops, Food Crops, Fruit and Vegetable Products, and Naval Stores), and one Laboratory (Engineering and Development) for engineering research and development.

Headquarters of the Division are located at the Southern Regional Research Laboratory, New Orleans, Louisiana. The Division also has personnel and laboratory facilities at Winter Haven and Olustee, Florida; Weslaco, Texas; Raleigh, North Carolina; Knoxville, Tennessee; and Natick, Massachusetts.

EXAMPLES OF OUTSTANDING ACCOMPLISHMENTS

Test Packs of Pure Culture Fermented Pickles Evaluated by Industry

Pure culture fermentation has been called the first breakthrough in the basic process for pickling cucumbers and other vegetables in more than 4000 years of pickle history. Eight companies, including several giants of the food processing industry, have put up test packs of pure culture pickles in institutional-sized containers or plan to do so this season. Industrial representatives have scheduled a short course to teach other pickle packers how to apply the new procedure commercially.

This improved fermentation process enables the industry to improve quality, offer new products, and reduce costs. Other advantages include control of bloaters and other defects in brine-stock pickles, better sanitation, and fewer disposal problems with salt and acid wastes. Most important, however, is that flavor characteristics of the final product can be tailored by selecting the type of cucumber and lactic acid bacteria.

In the age-old method of pickling in vats, fermentation depends on lactic acid bacteria that enter the brine solution by chance. However, in the controlled process developed by the Division in cooperation with the North Carolina and Michigan Agricultural Experiment Stations and Pickle Packers International, Inc., the undesirable and interfering naturally occurring microorganisms are inactivated. The cucumbers are washed, heat treated, packed in containers, seasoned with spices, and then covered with a pasteurized acidified salt brine. Each container is inoculated with the bacteria culture desired and then sealed. In contrast to the lengthy conventional method, the new pickling process is complete within a week, although flavor continues to develop for a longer period. The method can also be applied to carrots, string beans, okra, and other vegetables and to Spanish-type fermented green olives.

PURE CULTURE FERMENTATION



A VERSATILE NEW PROCESS FOR PICKLING

CUCUMBERS AND OTHER VEGETABLES

DELICIOUS, NUTRITIOUS ORANGE JUICE TABLETS



NUTRITIVE ADVANTAGES OF ORANGE JUICE

BUT

NO REFRIGERATION OR RECONSTITUTION

Orange Juice Tablets--A New Citrus Product

A small, flavorful orange disc that can be eaten like candy may offer a new outlet to citrus processors and a new product to a wide variety of consumers. Developed by Division scientists in cooperation with the Florida Citrus Commission, the tablets are prepared from concentrated orange juice that is dehydrated and pressed into any desired shape or size. Since they consist almost entirely of natural juice solids flavored with enrobed orange oil, they have all the nutritive advantages of orange juice, including caloric content, vitamin C, other vitamins, and minerals. Similar tablets can also be prepared from grapefruit and from various combinations of citrus and berries. In fact, the process appears to be applicable to almost any kind of solid with high sugar content.

With advice and assistance from USDA on the compression and manufacture of tablets, one company has developed several new products from orange, pineapple, grapefruit, blueberry, and raspberry. These products are being sold to a number of manufacturers of pie, cake mixes, and similar products.

Moreover, since the tablets have diverse potential uses, not only food and candy companies but even pharmaceutical companies have expressed interest. In addition to attracting markets as a nutritious convenience food and as a confection, they are of course ideal for consumers in specialty markets, such as campers, dieters, or military field units. They also offer a means for citrus to compete in fields now dominated by synthetic materials.

Improved Durable-Press Cottons Produced by Steam Set Process



A new process--Steam Set--developed by Division scientists has good potential for the commercial production of improved durable-press cotton apparel and thus is evoking considerable industrial interest. Already successfully applied on a mill scale, this process is currently undergoing further commercial-scale testing and development. It utilizes a combination of readily available chemical agents, which are set in the cotton fabric by a steaming procedure. The process is efficient and versatile, being adaptable to both types of durable-press processing, i.e., pre- and post-cure.

In comparison with conventional durable-press cotton goods, Steam Set fabrics have significantly higher breaking and tearing strengths and abrasion resistance and thus greater durability and longer wear life. Steam Set should

be particularly suitable for the production of ladies' and children's durable-press goods and men's durable-press trousers, suits, and colored shirts. These products utilize a significant portion of the approximately 2.6 billion yards of textiles annually treated for durable-press applications.

New Rosin Derivatives Produced Commercially for Use in Adhesives

Division scientists have recently produced several new rosin derivatives with good industrial potential in the adhesives field. Particularly promising are polyester products made from rosin modified with acrylic acid; they are useful in at least three major areas of adhesives--rubber tackifiers, pressure-sensitive adhesives, and hot-melt adhesives.



A resin manufacturer is already advertising two of these new rubber tackifiers for sale, and a potential user anticipates a starting market of over three million pounds annually. The excellent qualities of the various rosin derivatives--good adhesion, versatility, attractive cost--should make them strong competitors in the large adhesives market, which currently totals about one billion pounds per year.

COTTON

Problems and Objectives

Synthetic or "manmade" fibers have aggressively encroached on cotton's markets, gradually reducing its share of the total U.S. mill consumption of textile fibers. In addition, U.S. capacity for producing cotton can far outpace consumption; even with acreage restrictions, production has frequently exceeded domestic consumption plus exports. Compounding these problems is the fact that some of the crop consists of lower quality cottons that are difficult to process; the resultant higher manufacturing costs more than offset the lower cost of the raw cotton. To help solve these problems, utilization research is directed toward the development of fundamental information and technology required for the production of new and improved cotton products to retain present markets and open new ones for this natural fiber.

Major objectives of the research are to develop:

1. Fundamental knowledge of the composition, structure, and properties of native and modified cottons.
2. New or improved techniques and machinery for mechanical processing of cotton.
3. Chemical and physical modifications and treatments to create new or improved cotton products for various end uses.
4. Flame-retardant cotton products to help protect the consumer and reduce loss of property from fire.
5. Methods for reducing stream and air pollution that may result from the processing of cotton textile materials.
6. Improved techniques for consumer care of textiles to improve service life and to safeguard health.

Progress

NEW AND IMPROVED TEXTILE PRODUCTS

A. Chemical Composition, Physical Properties, and Structure

1. Relationships of the Structural Arrangements Within Cotton Fibers to the Physical and Chemical Properties of Native and Modified Cottons. Research investigations of the morphology of cottons crosslinked or graft polymerized by vapor treatments have continued. Microscopical observations were made on a series of cottons reacted by vapor phase in a closed, constant pressure reactor using various amounts of formalin and sulfur dioxide. Samples having formaldehyde contents ranging from 0.62% to 0.22% and wrinkle recovery angles

of approximately 300° to 260° were reacted throughout the fiber body, as shown by insolubility of both whole fibers and thin sections of fibers in 0.5M cupriethylenediamine hydroxide. Treatment in this type of reactor resulted in samples being reacted throughout the fiber body, whereas treatment with the same reagents in an open, constant volume reactor of previous experiments resulted in mostly peripheral crosslinking in the fibers.

Electron microscopic examination of cotton treated with various swelling agents revealed differences due to the nature of swelling at the microfibrillar level which could be correlated with other fine structure parameters. A water-soluble embedding medium was standardized to embed the fibers in wet and swollen state directly after the swelling treatment. If used appropriately as a swelling agent, Triton B may prove to have potential for improving the crease recovery and mechanical properties of cotton. Electron diffraction techniques used to evaluate crystallite orientation show cellulose orientation to differ significantly between ramie and cotton even at the subfiber fibrillar level. Gas adsorption studies show accessible void volume of cottons to be a function of various swelling or crosslinking treatments, but most significant changes in void morphology correlate only with change in crystal structure. Only two reagents, stearoyl chloride and tris(1-aziridinyl)phosphine oxide, caused changes in energy of accessible void surface.

Cotton yarn swollen with 40% aqueous benzyltrimethylammonium hydroxide (BTOH) was found to react four times as fast with 1,3-dichloropropene as did yarn swollen with mercerization-strength (23%) sodium hydroxide. The decrystallizing effect of BTOH on cotton appears responsible for this increased rate of reaction and crosslinking at room temperature. Cotton yarn decrystallized with BTOH and then treated with polar organic solvents underwent sizable gains in weight, and the cellulose I crystal lattice was converted to cellulose II lattice. Formation of inclusion complexes between decrystallized cotton and the polar solvents was indicated. BTOH-decrystallized yarn treated with mercerization-strength alkali metal hydroxides underwent further swelling and shrinkage. The washed and dried yarns retained a high degree of stretch. A low degree of tension placed on slack, soda-cellulose yarn and maintained during washing and drying produced a large increase in strength retention after subsequent crosslinking.

Cotton fibers grown in controlled environments and harvested before maturity showed decreasing weight loss when treated with an enzyme preparation (an indication of cellulose accessibility) as the cotton boll approached maturity. Similar trends were found in measurements of deuterium exchange. Fiber density increased with increasing maturity. Density of "mature" fibers from bolls harvested after opening decreased as average growth temperature decreased. Methods for determining accessibility by deuterium exchange and by iodine sorption were perfected.

In a P.L. 480 project at the Central Laboratory, T.N.O., Delft, Holland, the influence of yarn geometry on the response of the structural elements of chemically treated cottons to stress and deformation is being investigated.

Samples of yarns previously studied in the raw state have now been chemically modified. Investigations included the effect of chemical modification on relative fiber mass per yarn cross-sections, yarn geometry, and response of the yarns to various stress parameters. Data derived from these studies will be compared with parallel data on the raw yarns, and the effect of the chemical modifications will be evaluated.

2. Adsorption and Swelling Phenomena in Native and Modified Cottons. The sorption and swelling abilities of cotton yarns variously processed with crosslinking agents and/or surface reactants were determined in terms of the alkali centrifuge value (ACV). The samples included cured products from recommended levels of reactions for achieving smooth-drying properties in cotton fabrics and from intermediate processing stages or levels of reactions. Parameters of the preparatory processes, such as curing time, catalyst, and procedure, influenced the level of ACV. Comparisons of pre- and post-test moisture regains were indicative of the accessibility of intrafiber regions to the 15% sodium hydroxide solution of the test and, therefore, of the relative alterations in cellulose crystallinity by the mercerizing action of the caustic solution. Weight losses after the alkali centrifuge test plus neutralizing-washing-drying procedures suggest varying susceptibilities of the treated yarns to the caustic action. The direct but curvilinear relationship found between ACV and yarn tenacity indicated that both properties were dependent upon the alteration of intrafiber structure by the presence of the crosslinks.

Other research showed that cotton treated by a wet-fixation step followed by dry-cure processing was not significantly different in surface area from that treated by the first step only. In contrast, large differences were observed between products from the pad-dry-cure process and the Form W formaldehyde type process. Porosity analyses indicate that loss of area occurs in the smallest-diameter pores.

Investigators at the Shri Ram Institute for Industrial Research, Delhi, India, have made further progress in a P.L. 480 research study of moisture sorption and desorption by crosslinked cotton as related to the state of swelling under which the cellulose is crosslinked. Moisture sorption and desorption over the range of 10 to 90% relative humidity was determined for cotton crosslinked by formaldehyde treatments that swelled cotton from 2.5 to 19% during crosslinking. Treatments that swelled cotton 7% or less gave moisture regain somewhat less than that of the control cotton, whereas treatments that swelled cotton 14% or more gave significantly higher regain. The regain for cotton fabric treated with formaldehyde in the vapor phase was about equal to that of the control; in contrast, the regain for cotton crosslinked in the collapsed state (high-temperature oven cure) was significantly lower. Similar moisture sorption and desorption data were also obtained for cotton fabric crosslinked with 1,3-dichloropropanol, epichlorohydrin, divinylsulfone, bis-(2-hydroxyethyl)sulfone, dimethylolethyleneurea, dimethylolurea, tris(1-aziridinyl)phosphine oxide, and potassium acid di(2-sulfatoethyl)amine. Agents that introduced crosslinks while the cellulose was swollen yielded

fabrics with regain higher than that of the controls; however, if crosslinks were introduced while the cellulose was collapsed, the fabrics had lower regain. Possible rupture of the primary wall of fibers in systems containing more than 65% water and 10% hydrogen chloride was suggested.

3. Mechanisms of Damage to Cotton by Chemical Actions. Research on the nature and mechanism of the chemical effects of ultraviolet light on cotton cellulose and related compounds was conducted under a P.L. 480 project at the University of Salford, Lancashire, England. The relationship between the fading and phototendering of anthraquinonoid vat dyes, Caldeon Yellow GN, 5GK, and 4G on cotton cellulose was examined. The mechanism by which formation of the leuco dye and photodegradation occur in visible light is comparable with the mechanisms elucidated for anthraquinone sulfonates in solution and on cellulose. Thus, proton abstraction by the excited non-aggregated dye occurs here also. Electronic energy transfer to cellulose, in competition with this abstraction process, would be favorable during ultraviolet irradiation and is the mechanism suggested under these conditions for the degradation of cellulose. The abstraction process probably occurs to a lesser extent in the dye system, due to a greater degree of aggregation of the dye. Accordingly, photolysis of the solid state cellulosic systems involving anthraquinone sulfonates is regarded as only a partially adequate model for the true dye systems. A different process operates when cellulose is irradiated with ultraviolet radiation as compared with visible radiation.

In a P.L. 480 project at the University of Bombay, India, research was continued to investigate the inhibition of the photochemical degradation of cotton by chemical modification and deposition of inorganic and organic compounds. Partially benzhydrylated cotton showed maximum degradation on exposure to light. Partial benzoylation resulted in a marked reduction of degradation by light. Experimental evidence was provided to support a proposed mechanism of photosensitization of cotton in the presence of an active vat dye. There is evidence that protection against damage by light is obtained, in part, by changes in the fine structure of cotton occasioned by certain chemical treatments. Nickel and chromium hydroxides afforded protection against damage by light. Pigments afforded protection in the following decreasing order: Titanium dioxide (nitrile), Chrome Oxide Green, Phthalocyanine Blue, Scarlet Chrome, Phthalocyanine Green, Toluidene Red, and Pigment Green B.

4. Structural and Compositional Changes Occurring During Chemical and Physical Modification of Cotton Cellulose. Polarized and nonpolarized infrared absorption spectra of cellulosics exhibited significant changes in both intensity and frequency on cooling. Absorptions in the OH stretching region shifted to lower frequencies, indicating increased intermolecular hydrogen bonding. The cellulose II spectrum showed evidence of intramolecular hydrogen bonding not present in cellulose I. Shifts to higher frequency occurred in the $1800-300\text{ cm}^{-1}$ region at low temperature. All bands that shifted on cooling were assigned to some type of vibration affected by changes in hydrogen bonding. Since absorption bands in the spectra of

samples containing no hydroxyl groups, such as cellobiose octaacetate and cellulose triacetate, did not shift with temperature, the shifts observed on cooling were undoubtedly associated with hydrogen bonding effects. This technique possesses great potential value for applications to the study of the hydrogen bonding characteristics of celluloses partially or completely substituted at specific sites on the molecule. Knowledge of the history of a fabric obtained by application of a method developed for the identification of additives on durable-press fabrics will permit the finisher to select optimum conditions for treatment.

The response of crosslinked cotton cellulose to alkaline swelling agents, as measured by changes in the extent and type of crystalline order, has been found to vary with the degree of crosslinking, the chemical nature of the crosslink, the state of swelling of the cellulose during the crosslinking process, and the swelling power of the alkali solution. Cellulose cross-linked with formaldehyde did not lose bound formaldehyde on exposure to strong alkaline solutions, but there was a significant decrease in nitrogen and formaldehyde contents of cottons treated with dimethylolethyleneurea or dimethylol carbamate. Tris(1-aziridinyl)phosphine oxide (APO) treatments were stable toward alkali. Resistance of all of the crosslinked cottons to change in crystalline character diminished as the stronger swelling agents were used; in most cases, a limiting state of disorder was reached in which only 30% of the cellulose exhibited crystalline order. The inherent lability of crosslinked cellulose structures to strong alkalis must be allowed for in commercial practice involving these agents.

An improvement has been made in the computational technique employed in the calculation of the population of sorption states of the protons in water-cellulose systems. The new technique eliminates the requirement that the line shapes of the various spectra be similar. An algorithm has been developed which permits the division of the spectrum of wet cellulose into interchanging and noninterchanging proton components by digital computer. This replaces the previous method that required special analog computers and involved considerable subjective judgment. Spectra are being obtained of celluloses with a range of sorbed water concentrations, and analysis of these spectra is in progress. A Wang Model 380 computer system is being used to perform the various calculations necessary in the analysis of wide-line nuclear magnetic resonance (NMR) spectra. Programs have been prepared to calculate the second moments, spin-spin relaxation time, and area under the NMR absorption curves. Analysis of data obtained thus far would seem to indicate that the techniques developed provide useful new information on water-cellulose sorption systems.

Other basic studies have clarified several aspects of the chemistry of cotton cellulose that are pertinent to the finishing or crosslinking of cotton fabrics--for example, to improve strength, resilience, and other end-use properties of the fabrics. The relative reactivities and accessibilities of the various hydroxyl groups of cotton cellulose in a reversible reaction have been determined. This knowledge should be useful in the

development of optimum performance properties in chemically modified and crosslinked cottons. Chemical evidence obtained in this research indicates that reactions of cellulose conducted in nonmercerizing media take place on the surfaces of microstructural units and that the individual types of hydroxyl groups exhibit selective accessibilities on these surfaces. The extent of selective accessibilities and of surface reactions on the microstructural units is related to the swelling strength of the reaction medium. Physical performance properties of selected crosslinked fabrics have been related to the extent of distribution of crosslinkages in the microstructural units.

Techniques have been developed for the application of gas-liquid chromatographic analysis to studies of selected acidic textile treating solutions. By use of these techniques, it has been found that 1-methoxymethyl-3-methyl-2-imidazolidinone is hydrolyzed in acidic solution to 1-hydroxymethyl-3-methyl-2-imidazolidinone, which is subsequently condensed to methylenebis-1-[3-methyl-(2-imidazolidinone)]. Gas-liquid chromatography has shown that the latter compound is produced directly from acidic solutions of 1-hydroxymethyl-3-methyl-2-imidazolidinone. Using similar chromatographic techniques, reaction rate constants have been determined for the disappearance of both the methoxy compound and the hydroxy compound at 4 different acid concentrations and at 2 different temperatures. The consumption of the methoxy compound follows first order reaction kinetics, whereas that of the hydroxy compound follows second order reaction kinetics. The hydrolysis of the methoxy compound appears to be a more rapid reaction than is the condensation of the hydroxy compound.

Tris(2-chloroethyl)phosphoramide was prepared for the first time. Cotton crosslinked with this compound showed moderately high wrinkle recovery angles. The actual degree of substitution was low in proportion to the add-on, indicating that the ratio of crosslink formation to polymer formation was small. Cotton fabric was crosslinked with N-methylbis(2-chloroethyl) amine and N-methylbis(2-sulfatoethyl)amine to yield identical substituents and crosslinks. Hydrolysis of the crosslinked samples and analysis of the hydrolysate showed that the simple crosslinks accounted for a minor fraction of the reagent residues. Simple substituents were next in abundance. Complex reaction products comprised the major component. The distribution of substituent groups in the 2-O-, 3-O- and 6-O-positions in untreated cotton cellulose and in hydrocellulose reacted with N,N-diethylaziridinium chloride indicates that the accessible disordered regions in cotton account for only about 10% of the total accessible D-glucopyranosyl units and that the accessible surfaces in crystalline regions account for the remainder.

Alpha and beta methyl D-glucosides were reacted with N,N-diethylaziridinium chloride in sodium hydroxide solutions ranging in normality from 0.1 to 6.0. The ratio of 2-O- to 6-O-substituents decreased with increasing base concentration, indicating that hydrogen bonding and complex formation play important roles in the reactions of carbohydrates. Formaldehyde-crosslinked

disordered (ball-milled) cotton was digested with cellulase. The rate of degradation was found to decrease as the concentration of glucose and cellobiose increased. By replacing the enzyme solution with fresh solution every 24 hours, 96% of cotton crosslinked by the Form W' formaldehyde process could be solubilized in 5 digestions. The extent of solubilization of cotton crosslinked by the Form C and Form D processes was 68% and 51%, respectively, in 5 digestions. The solubilized portion was subjected to paper chromatography. Two formaldehyde-containing fractions were separated: one appeared to be crosslinked cellobiose; the other, crosslinked oligosaccharides.

The gel permeation technique has been used to measure differences in the alteration of pore volume and pore size distribution produced by crosslinking cotton fabric with formaldehyde under various conditions. Products cross-linked in a water-swollen state were markedly different from those reacted in a semi-collapsed state or under curing conditions where there was a fully collapsed cellulose structure. Quantitative measurements of the two determinable parameters--internal solvent volume and permeability limit--are indicative of changes in the distribution of pore volume between larger and smaller pores. The reactions were applied to cotton in fabric form, and both unmodified and crosslinked samples were reduced to the size required for packing chromatographic columns without loss of crystallinity. Mercerization of Wiley-milled fibrous cotton increased the total pore volume but slightly decreased the maximum pore size. Basic investigation of the gel permeation process indicates that the measurements are empirical, yielding relative values for the two parameters determined.

The Form W' process for crosslinking cotton with formaldehyde was shown to degrade the cellulose molecule severely. With increasing time in the acidic bath (14.6% hydrochloric acid), formaldehyde content of the cotton increased; however, the average molecular chain length (viscometric) decreased greatly, and the molecular-weight distribution curves also indicated shifts in chain length and in the proportions of chain lengths. The extensive computations involved were processed entirely by computer. Tear and breaking strengths, elongation, and flex abrasion showed very rapid linear decreases with the reciprocal of viscosity chain length up to a point after which the rate of decrease changed markedly. This being a room temperature reaction, molecular cleavage comes only from the acid catalyst. Further conclusions relative to strength losses require more knowledge of the ratio of competing reactions of chain cleavage and crosslinking and of the distribution of crosslinks in the fine structure of the cotton fiber. Nitration is required to prepare a soluble sample. Results indicate that some crosslinking may be retained in the solubilized samples without affecting solubility.

Researchers at the Swiss Federal Institute of Technology, Zurich, Switzerland, have completed a P.L. 480 research study of the chemistry and structural nature of the bonds formed between formaldehyde and cellulose in formaldehyde-treated cottons. A reliable method was devised for

determining formaldehyde in cellulose formals and in methylated cellulose formals. New permethylation processes that work without elimination of formaldehyde from the cellulose formals were developed and applied in structural studies. The distribution of linkages of formaldehyde to cellulose has been determined for cellulose formals prepared by a variety of processes, and the average length of these linkages has also been estimated. The reactivity sequence of the hydroxyl groups of the D-glucopyranosyl units was generally C-6>C-2>C-3, but in several cases the reactivity of C-3 was greater than that of C-2. The average length of the linkages varied between 1.0 and about 2.3. Estimates were made relative to the amount of intraglucosidic formal rings (C-2 to C-3) developed in the various cellulose formals. Relationships were established between the foregoing structural features of the cellulose formals and the performance characteristics of the fabrics.

5. Methods and Instruments for Measuring the Physical Properties of Cotton and Its Products. In research to correlate abrasion tests with service wear of all-cotton durable-press fabrics, it has been found that the mechanisms causing abrasion damage on trouser cuffs made from such fabrics are different for top-loading, agitator-type home washing machines and side-loading tumble dryers. In the washer, damage occurs first at the center seam area; in the dryer, it occurs first at the cuff tip. Some of the physical properties of the fabrics correlated with results of laundry abrasion tests. However, correlations between laboratory abrasion tests and physical property tests were generally not very good. Evaluation of actual in-service wear damage was found to be very complex. Abrasive wear on similar areas of work trousers for different wearers showed patterns different from each other and none showed any apparent agreement with laboratory tests.

Abrasion damage obtained on all-cotton durable-press trouser cuffs subjected to washing and tumble drying cycles in home laundry equipment was significantly affected by the weave construction of the fabric. A fabric with a tighter weave construction experienced abrasive damage sooner than a similarly treated fabric with a looser weave construction. Results also showed that increasing the wash load decreased the rate of damage obtained at the center seam area of the cuff but increased the rate of damage obtained at the cuff tip. In-service wear testing of trousers made from a sateen construction given durable-press treatments was discontinued because of difficulty in determining differences in wear damage among the different treatments. Wear testing of men's durable-press commercial dress shirts showed that wearing contributed additional abrasive damage to the shirts over that of laundering alone. The results indicated satisfactory service for all shirts studied, with a polyester/cotton blend shirt having an edge over the all-cotton shirts in durability to wear.

Fundamental research on the geometry of wrinkles as they affect the rating of acceptability of wash-wear cotton fabrics was continued in a P.L. 480 project at the Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry of the State of Israel. A reliable system incorporating the principles of the voltage transducer to trace the contours

of fabric wrinkles was developed and used to describe the surface of wrinkled fabrics. A computer section of the system translates the electrical data to indicate wrinkle parameters, such as height, slope, and density. An 8 mm movie film was prepared that depicts the apparatus, how wrinkles are formed, and the manner in which the wrinkles are measured. Several fabrics of different constructions were woven to study the effects of textile structure on wrinkling. The fabrics were evaluated by the system after laundering and after wrinkling by various laboratory test methods such as the TEFO conic wrinkle tester, the Celanese wrinkle tester, the AKU tester, and the Launder-O-Meter. The AKU tester and the Launder-O-Meter afforded more reproducible results than those obtained by laundering or by either of the other two laboratory testers.

In contract research at Stanford Research Institute, Irvine, California, the instrument previously developed by the contractor for USDA-ARS to count neps in cotton at various stages of processing is being redesigned to separately count neps and particles of trash and other foreign matter. A two-color illumination and optical system using monochromatic light and appropriate filters has been designed and tested for this purpose. The bench model apparatus successfully distinguishes between neps and trash particles, and can even separate the neps into three categories of physical size. Research is underway to improve the sample feeding mechanism, and to evaluate the instrument on raingrown and irrigated cottons. The availability of the finished instrument will aid cotton gins and textile mills to adjust processing equipment for maximum trash removal without damaging the fibers, and thus to improve cotton product quality.

The same contractor (Stanford Research Institute) has established the principle, design, and operating technique of measuring length and diameter of textile fibers by optical means. It has been proved that "forward-scattered" light from fibers illuminated in a high speed air stream can be collimated and measured to provide a quantitative assessment of fiber length parameters. The mechanism for exposing a predetermined number of straightened cotton fibers to the measuring element and the electronic counting and readout systems have been evaluated and found to perform satisfactorily. Delivery of the instrument by the contractor is being delayed by difficulties in developing a means for extracting single fibers from a mass of fibers and feeding these to the measuring system. The successful development of an instrument for measuring single fiber length and diameter parameters will assist geneticists in breeding cotton with desired length characteristics, machinery manufacturers in developing improved ginning and textile processing equipment, and textile mills in producing higher quality products.

B. Chemical and Physical Investigations to Improve Products

1. Exploratory Chemical Modification and Finishing of Cotton.

Tris(p-chlorophenyl)sulfonium chloride has been prepared and found to crosslink cotton yarn in the presence of alkalies. The ease of preparation

and water solubility of this sulfonium salt make it of interest as a possible wrinkle-proofing agent for cotton. A commercial product containing triphenylsulfonium chloride as the major ingredient appears to contain the tris(chlorophenyl) analog as an impurity, and the increased wet wrinkle resistance the commercial mixture imparts to cotton fabric may be due to this impurity. Zinc chloride and ferric chloride complexes of tris(p-chlorophenyl)sulfonium chloride have been isolated and characterized.

Cotton printcloth has been treated with thionyl chloride to produce chlorodeoxycellulose fabric. Chlorine contents of 1.2-4.4% were obtained with little loss of tearing strength or flex abrasion resistance. Treated fabric was readily crosslinked with dimethylolethyleneurea to produce high wet and conditioned wrinkle resistance. Cotton yarn treated with thionyl bromide was found to be moderately flame resistant and to contain considerable sulfur but little bromine. The reaction of trichloroacetonitrile with cotton yarn in the presence of alkalies gave a highly amorphous yarn, as shown by x-ray diffraction. The yarn contained cellulose trichloroacetimidate--trichloroacetate mixed ester. Osnaburg cotton fabric underwent 18-32% weight gains when treated with trichloroacetonitrile. The fabric acquired moderate flame- and wrinkle-resistance durable to repeated laundering.

Cotton cellulose fabrics were esterified with cinnamoyl chloride and then irradiated with ultraviolet light. The irradiation caused the formation of crosslinks in the fabric by the photodimerization of the substituent groups. The increase in wrinkle recovery angle and the number of crosslinks in the fabric were studied as functions of the time of irradiation and the degree of substitution of cinnamate groups in the fabric. The use of polycarboxylic acids as curing agents and additional crosslinking agents for standard wet-fixed cotton fabrics was studied as a means of permanently attaching catalytic groups to the fabric in order to permit recurring or recreasing of the fabric in finished garments. Citric acid and cyclopentanetetracarboxylic acid can serve as curing agents in wet-fixed cotton fabrics, giving results equivalent to those obtained with magnesium chloride in terms of both wrinkle recovery and strength retention. Trimethylene-trisulfone and formaldehyde were found to react with cotton cellulose and basic catalysts to give high add-ons, but no increase in wrinkle recovery was observed. *s*-Trithiane did not polymerize in cotton cellulose fibers. The kinetics of the dissociation of di-*tert*-butylcyclopentadiene were measured.

The thermal analyses for the dissociation of the 2-, 3-, and 4-N-pyridyl-carbamylated cotton fabrics have been completed. Kinetic investigations demonstrated that the 2- and 4-derivatives are preferred for thermally reversible crosslinking; entropy considerations favor the latter. However, catalysis by the organic base (pyridine) of the degradation of the cotton substrate itself makes this system unattractive. Another organic base-reacted cellulose--diethylaminoethyl (DEAE) cotton--was investigated via thermal analyses. Although a loss of diethylaminoethyl alcohol at low

temperature was observed, the major portion of the organic base was retained up to temperatures approaching cellulose decomposition. The use of DEAE groups on a cellulose substrate as a built-in catalyst for relocation of base-sensitive crosslinks has been demonstrated. Therefore, an investigation of the thermal behavior of one such system, that of beta-aminoethyl vinyl sulfone derivatives of untreated and DEAE cottons, was initiated. Preliminary results suggest that thermally induced reversible crosslinking is prevented by the increased thermal stability of the product.

Diethylaminoethyl (DEAE) cottons in fabric form were prepared in organic solvents, and these weak base exchangers were converted directly to strong base anion exchangers. The amino groups of these exchangers were used as in-situ catalytic sites for the subsequent reaction of cotton with various heterocyclics such as epoxides, anhydrides, and ethyleneureas. Acid salt forms of DEAE-cottons proved effective in delayed-cure processes for producing durable-press cottons. In other work, cotton fabric of cellulose I crystalline lattice and a premercerized fabric of a mixed cellulose I and II lattice were reacted with alkoxides of Group IA metal ions in various alcohols to form alkali metal cellulosates. Conditions for the most efficient preparation of these metallic cellulosates and for their subsequent reactions with a variety of heterocyclic compounds were established. Properties of cotton fabrics finished with a given heterocyclic in non-aqueous media were compared with properties of fabrics finished with the same reagent in water.

In contract research at Gulf South Research Institute, New Orleans, Louisiana, the wrinkle recovery of polymer-coated cotton printcloth was generally found to correlate closely with the elastic behavior of the polymer film. Of the several tensile parameters that can describe elasticity, immediate strain and work recoveries and stress decay were found to be the most sensitive indicators of the polymer's performance on the fabric. Delayed (or total) recovery, ultimate elongation or permanent set were found to be important but were less sensitive parameters, whereas tensile strength and initial modulus appeared to be unrelated. In addition to these elastic properties of the polymer, the coupling that occurs between the polymer recovery forces and those of the fabric also contribute to the ability of the fiber assembly to recover from distortion. Thus, certain highly elastic polymers, polysiloxanes, for example, do not develop the degree of resilience on treated cotton fabrics expected from evaluation of tensile parameters of the film and considerations of similar data from other polymers such as the polyacrylates. These data should assist industry in the design and application of polymer systems to cotton to achieve enhanced resilience of the fabric.

Contract research at New York University, Bronx, New York, to investigate polymer encapsulation of cotton fibers has been completed. Experiments on the application of polyamide resins onto the surfaces of cotton fibers by in situ interfacial polymerization reactions at near ambient temperatures were continued. Additional studies relating to the diisocyanate-crosslinking

of Nylon 610 polyamide-coated cotton fabrics were conducted and the properties of the resulting cotton fabrics evaluated in terms of selected pertinent performance parameters. Typically, at 4% add-on of Nylon 610 polymer with 5% trimethylhexamethylene diisocyanate loading, Monsanto wrinkle recovery values in the 260-270° range were obtained with 75% strength retention without decreasing the abrasion resistance. The contractor also investigated the free radical initiated vapor-phase polymerization of ethyl acrylate monomer onto the surfaces of cotton fibers and subsequent crosslinking thereof with a methylolamide crosslinking agent. Fabric properties were measured and found to be similar to those determined for diisocyanate-crosslinked Nylon 610 coated cottons.

Cotton yarn decrystallized with benzyltrimethylammonium hydroxide (BTOH) underwent recrystallization to cellulose I if washed with water. When the decrystallized yarn was treated with mercerization-strength alkali metal hydroxides prior to washing, the yarn underwent only partial recrystallization and yielded cellulose II together with a stabilized, amorphous form of cotton. When the yarn was given this dual pretreatment under tension, it retained higher tensile strength after crosslinking than when pretreated with either BTOH or alkali metal hydroxide alone under tension and then crosslinked. Addition of small concentrations (1-5%) of BTOH to liquid ammonia, hydrazine, or ethylenediamine greatly increased the plasticizing action of these agents on cotton, permitting durable false twist to be imparted to yarn. Tensioning, crystallite reorientation, and lattice rearrangement have been carried out on cotton swollen in liquid ammonia, in searching for forms of cotton especially suited for crosslinking. A new complex of cellulose with 1,2-propanediamine was prepared and studied by x-ray diffraction.

2. Chemical Reactions Initiated in Cotton Cellulose and Chemically Modified Cotton by High-Energy Radiation, Light and Heat. Kinetics and mechanisms of radiation-initiated polymerization of binary monomer mixtures and of water-soluble monomers with cotton cellulose were determined. Photo-irradiation of cotton with near-ultraviolet light initiated free-radical formation with minimum degradation. Cotton thienates and furoates were prepared and characterized for antimicrobial and radiation resistance. Stabilization of free radicals generated in redox systems by reaction with transition metal ions was observed, as related to bleaching, weathering, and polymerization reactions of cotton. The wash-wear rating for all-cotton durable-press twill was improved from 4.1 to 4.3-4.7 after 30 wash-dry cycles by blending fibrous cotton copolymers with cotton fibers. Soil-release durable-press products were prepared by radiation-initiated copolymerization of methacrylic acid with cotton. (Estimated chemical costs are 0.5 to 1.3 cents per sq. yd. of printcloth.) Grafting of ethyl acrylate onto cellulosic fibers imparted elastomeric properties to the products. Reaction of tung oil with cotton increased abrasion resistance and wrinkle recovery. 5-Bromo-N,N-pentamethylene-2-furoamide, -N,N-pentamethylene-2-thioamide, and -2-thiophene-N,N-pentamethylene acryloamide were prepared during synthesis of cellulose products.

An investigation of the preparation of radioresistant and radiosensitive celluloses was continued under a P.L. 480 grant at the Cotton Technological Research Laboratory, Bombay, India. The effects of high energy radiation on the properties of cotton in the presence of methanol, isopropanol, butanol, ethylamine, diethylamine, triethylamine, di-n-propylamine, piperidine, piperazine, aniline, diphenylamine, triphenylamine, formic acid, acetic acid, glucose, indole, urea, water, 2,6-di-*tert*-butyl-p-cresol, or anisole were investigated over a range of experimental conditions. In general, all of the amines showed some radioprotective effect for cotton; ethylenediamine had the greatest effect. For the aliphatic amines, radioprotective effects for cotton increased with an increase in the concentration of amine groups. For aromatic amines, radioprotective effects for cotton increased with increase in the concentration of phenyl groups in the amines. Indole showed a radiosensitization effect on cotton. Allylated cotton cellulose fibers, irradiated to low dosages, showed an increase in breaking strength of the yarns. Electron spin resonance spectroscopy is being used to investigate the free radical reactions initiated.

3. Mechanisms, Rates and Catalysis of Reactions of Cotton Cellulose and of Chemically Modified Cotton. Rates of reactions between cotton and selected mono- and dimethylolated ureas in organic solvents have been measured. Activation parameters have been calculated from the specific reaction rate constants for a series of temperatures. The rates and activation parameters for these reactions have been compared with those of corresponding reactions in aqueous media. The relative rates of reaction of cotton with these reagents and the relative rates of hydrolysis of fabrics finished with these reagents will supply information needed to elucidate mechanisms of reactions involved in preparation of durable-press cottons. Several organic solvents have been found to be suitable reaction media for the reactions of cellulose with N-methylolated ureas in the absence of external catalysts. Catalysts that produce durable-press cottons at relatively low temperatures have been found.

Researchers at the Ahmedabad Textile Industry's Research Association in India are conducting a study of the correlation between the structure and absorptivity of cotton crosslinking agents and their reactivity toward cotton. The crosslinking agent dimethylethyleneurea (**DMEU**) both ionized and associated in solution; the predominant action was determined by concentration. Monomeric DMEU was absorbed by cellulose from water, but aggregates were not. Absorption of DMEU, therefore, decreased sharply above a critical concentration near 45×10^{-3} moles per liter. The reaction between cotton and DMEU in water with magnesium chloride as a catalyst was initially first order with respect to DMEU. Maximum reaction occurred at pH 2.5. Because this is near the isoelectric point of cellulose, reaction with neutral hydroxyls of cellulose is suggested.

Partial cellulose esters (degree of substitution < 0.2) of selected monobasic and dibasic acids were prepared by various methods in aqueous and nonaqueous media. Changes in recovery from deformation behaviors of these esterified

cottons were correlated with observed differences in fine structures of the finished fabrics and with structures of substituents on cotton. Wrinkle recovery of cellulose esters and ethers were affected by type of crystalline lattice of cotton. In brief, it proved easier to improve the conditioned wrinkle recovery of cotton having cellulose I or IV lattices than of cotton having cellulose II or III lattices.

4. Exploratory Physical Investigations of Native and Modified Cotton. Measurements of single-fiber and fabric properties for cottons chemically modified to improve wrinkle recovery and abrasion resistance have shown that inter- and intra-fiber properties affect wrinkle recovery. In four semicommercial durable-press processes, larger differences in fiber properties occurred at intervals before rather than after completion of the processes. The differences indicated that wrinkle recoveries were occurring through slightly different mechanisms in the different processes. The wet-fix treatment produced the highest wrinkle recovery with the smallest increase in fiber tensile recovery. In other processes, high wrinkle recoveries were obtained with small increases in tensile recoveries when surfaces were altered or lubricated or fiber shapes changed. The decrease in strength with increase in recovery restricted the use of fiber recovery to levels below the maximum attainable by crosslinking. At intermediate fiber recovery levels, the restoring forces must be kept in a single direction through stabilization of the fabric. Comparable wet and dry wrinkle recoveries were found when fiber movements were small during wetting and drying of fabric. Computer programs were used in tensile property analyses.

The mechanism of crease formation and recovery in ease-of-care treated cotton fabrics was investigated further in a P.L. 480 project at the Swedish Institute for Textile Research, Gothenburg, Sweden. Basic analyses of fiber versus fabric recovery indicated that the features of elastic recovery are comparable in fibers taken from fabrics and in the resin-treated fabrics. Further studies of moisture during formation and recovery from wrinkling show that wrinkling is related to the moisture level when the wrinkle is formed and the hygroscopicity of the treated cellulose at different moisture levels. Crosslinks formed when fibers are swollen (moist crosslinking) have a flat moisture absorption isotherm and less dependency on atmospheric moisture during wrinkling. Repeated wrinkling at a single point is more definitive of durable-press characteristics than is recovery from single wrinkling as employed in crease recovery measurements as now usually performed. This observation is consistent with the performance characteristics of durable-press garments.

An investigation of the correlation between several important physical properties of cotton apparel fabrics and their performance in actual service tests was continued in P.L. 480 research at the Shri Ram Institute for Industrial Research, Delhi, India. Wear trials were extended to include industrial labor uniforms, shirts and trousers for civilian use, and women's domestic apparel. Garments with crease- and soil-resistant

treatments were evaluated. Service performance results showed good agreement with retained tensile strength and toughness for shirts and work trousers. Intensive salvage studies of worn-out garments showed that zonewise location of test specimens was extremely important in evaluating the garments' serviceability on the basis of retained levels of mechanical properties. The results indicated that tear failures were due mostly to local weakening caused by abrasive actions. Severe edge wear was observed when either the face or back of the fabrics was exposed with the filling yarns lying along the edge. Accelerotor test results for edge wear correlated well with service performance.

In other P.L. 480 research at the Shri Ram Institute for Industrial Research, mathematical models were developed for the prediction of fluid-to-particle heat transfer coefficient, overall heat transfer coefficient, solids holdup, pressure drops, particle surface area, and other heat and mass transfer parameters relating to the design of countercurrent fluidized bed units for the efficient drying and curing of resin-treated cotton fabrics. Previous studies concerned with the crosslinking of DMEU and APO resins with cotton using methods of conduction, convection, and co-current fluidized bed curing were extended to the countercurrent fluid bed. Results confirmed prior findings that fluid bed processing produces higher heat transfer rates and generally more efficient curing than conventional pad-dry-cure methods but does not effect any improvement of product quality. Very surprisingly, there was no apparent attrition of fluidized sand particles or particle carryover into the fabric.

An exploratory investigation of the taper of cotton fibers and its effect on processing characteristics is in progress in a P.L. 480 project at the South India Textile Research Association, Coimbatore, India. Fiber taper of seven varieties of cotton was studied by microscopic, gravimetric, and cut middles techniques. By the microscopic method, the width of the fiber profile was constant from root end to midpoint and then decreased to the tip. By the gravimetric method, the width decreased in both directions from the midpoint. Although results for the gravimetric method based on fiber bundles were generally comparable to those of the more tedious microscopic method based on individual fibers, the relationship was not particularly pronounced. The cut middles technique showed the linear density of the root and tip segments to be lower than that of the middle portion. A comparison of fiber properties showed that taper influences length and strength. An optical device has been built for use in measuring taper.

In P.L. 480 research at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, the effect of fiber properties on spinning drafting tenacity for both high and low spinning break drafts was studied. With the high break draft, fiber fineness had little effect on the spinning drafting tenacity. However, with the low break draft, fiber fineness did have an influence on the drafting tenacity. It was found that with spinning drafting tenacity and fiber tenacity as the two

independent variables, spinning drafting tenacity had a greater influence on the minimum spinning twist (an indicator of spinning end breakage), whereas fiber tenacity had a greater influence on yarn strength.

A P.L. 480 research study of the factors that affect drafting capacity, spinning efficiency, and yarn quality of the direct sliver spinning system was continued at the Ahmedabad Textile Industry's Research Association, Ahmedabad, India. The investigations were extended to the effect of total draft and draft ratios on yarn numbers 36/1, 40/1, and 44/1 as spun on the OMS direct spinning system using a 1-5/32" California cotton. It was found that the optimum draft ratios were 1.4, 1.5, and 1.6 for the 36/1, 40/1, and 44/1 yarns, respectively. Yarn strength increased with increase in total draft, reached a maximum, and then decreased rapidly with further increase in total draft.

Research to investigate the effects of atmospheric conditions during the spinning of cotton yarns on yarn properties and spinning efficiency is continuing in a P.L. 480 project at the South India Textile Research Association, Coimbatore. Substantially all of the work involving a medium staple length (1-1/16 inch) cotton has been completed. The experimental design employed for this work involves two yarn sizes, two drafts, two twist multipliers, and three spindle speeds (24 treatment combinations). Each of these spinnings is to be performed under ambient conditions covering seven levels of relative humidity at each of four levels of temperature. In general, spinning efficiency tended to be lowered by high temperatures in combination with low humidities and by low temperatures in combination with high humidities.

Fundamental investigations to obtain information needed to predict the performance of cotton yarns during weaving were continued in P.L. 480 research at the Fiber Research Institute, T.N.O., Delft, Holland. Data developed by use of the pilot-type loom were essentially verified on a large scale loom. Breaks due to increased abrasion caused by "joints" in the yarn resulting from imperfections, adjacent knots, or lint accumulation always occurred in the heddles or between the heddles and the cloth fell. It was found that over 50% of the piecings that were present in the warp were broken in the reed zone due to their having torn apart by the reed motion. As a result, the cause of the break could be unidentifiable or incorrectly classified. A break caused by contact between a thread and the shuttle occurred when a joint was formed in the front shed. With a damaged shuttle, the breakage risk was about twice as high. A momentary joint formation in the back shed caused one of the threads involved to break at the heddle eye at a tension below its normal breaking strength. Most of the breaks occurred in the zones of the cloth fell and just before the first harness. Of the 21 breakage causes evaluated, about 13% were attributable to spinning piecings, 28% were unidentified, and about 23% were attributable to dust sized to a thread, to loosened knots, or to breaks at the knot.

Further research on the factors that affect curling and bursting of pre-ponderantly warp- and filling-faced cotton fabric structures during processing of cotton into end-use products was conducted in a P.L. 480 project at the Bombay Textile Research Association, Bombay, India. Three drill constructions (heavy, medium, and light) were processed, tested, and completely analyzed. The parameters studied in this series were selvedge, strip length, crimp ratio, selvedge width, selvedge thickness, breaking strength, elongation at break, and both wet and dry twisting angles. Weaving and testing of plain-weave fabrics of medium construction have also been completed. By employing the data obtained in this work, parameters can be chosen to produce the ideal selvedge for these weaves so that a minimum of curling will result during their processing.

C. Technology--Process and Product Development

1. Improved Procedures for Mechanical Processing of Cotton. In continued research to increase the utilization of low and high Micronaire reading cottons of medium staple length, cotton mixes composed of various percentages of low, medium, and high Micronaire cottons and a control mix of average Micronaire cotton have been processed into printcloths which are now being chemically finished commercially. Yarn and preliminary gray fabric data indicated that some of the experimental fabrics woven from the high-low Micronaire reading mixes have yarn and fabric qualities comparable to those of the control lot. If the results on chemically finished fabric and market evaluation bear out this observation, it may be concluded that some of the high-low Micronaire reading blended lots will be suitable for printcloth manufacturing. In another phase of the investigation, six of the eight experimental sheetings and a control have also been woven and these also will be finished commercially. Physical property data from these yarns indicated that some of the experimental lots are equal in quality to the control lot. A similar investigation of denim fabrics has begun.

In completed complementary research under contract at Texas Tech University, Lubbock, textile processing methods have been developed to homogeneously blend short staple cottons differing extremely in Micronaire reading using conventional processing equipment and technology. Detailed procedures have been developed for processing such blends with acceptable processing efficiency. The fiber properties of extra-high and extra-low Micronaire short staple cotton complement each other, resulting in yarn properties equivalent in most cases to those of yarns produced from average Micronaire cotton. The research has shown that short staple, extreme Micronaire range cotton that sells for 2 to 4 cents/lb. discount can be used to produce yarns of a quality adequate for many consumer products. The results have a practical value in (1) creating a market for the farmers' cotton of this type, (2) reducing the cost to the government loan program for handling such cotton, (3) reducing manufacturing costs of textile mills, and (4) reducing consumer costs for a variety of end products.

New research by the same contractor (Texas Tech University) is concerned with the use of discount cotton in the development of fabrics for specific end-uses. From results of the earlier contract work, specifications for the 28 bales of cotton required in the research were established and the cottons purchased. The cotton has been opened, blended, cleaned, and stored in picker laps awaiting processing into yarns. A system has been devised to monitor the cotton blends in terms of differential dye sorption at the second or finishing drawing process. Practicability of weaving the following fabrics chosen for production on the contract has been established by the weaving of narrow widths: a 3/2 righthand twill denim and a Bedford cord, for the apparel trade; a bark cloth, for upholstery or drapery; huck toweling, for additional household items; industrial sheeting, shoe duck, a drill, and a canton flannel, for the industrial trade.

Other research on discount cottons is directed toward the development of methods for efficiently carding such cottons. Carding research has been conducted with low and high Micronaire reading discount cottons and a 50/50 blend of the two, using various sliver weights and production rates. The results indicate that to obtain more efficient processing and improved yarn quality for low Micronaire reading discount cottons, a lightweight card sliver should be used, whereas for high Micronaire reading discount cottons, either heavy or lightweight card sliver may be used. Sliver weight should be decreased as the amount of low Micronaire cottons in a blend is increased. The short fibers of cotton are the first to imbed in the card cylinder clothing, revealing the importance of developing efficient methods for the removal of short fibers at the card. The preliminary findings indicate two promising ways to improve the cylinder-to-doffer fiber transfer and thereby improve the carding of low Micronaire reading discount cottons, namely, raising the fibers by use of a suitable roll, and reducing the friction between the fiber and cylinder teeth by metallurgical or coating methods.

In further research to determine the interactions of process variables and product properties in high-speed cotton spinning, the effects of processing machine variables of the Rovematic roving and Spintester spinning frames on roving and yarn properties were studied. Maximum yarn strength was obtained with a 1-5/8" back-to-middle roll setting and a 1.4 break draft on the roving frame and a 2-1/16" back-to-middle roll setting and 1.6 break draft on the spinning frame. Differences in fiber parallelization in second drawing slivers of different weights were greatly reduced in subsequent rovings due to the higher roving draft required for the heavier weight sliver. Guides have been provided industry for properly combining sliver weights, roving drafts, fiber parallelization, and roving evenness to achieve improved yarn properties.

Mechanical methods for producing knitting yarns with improved physical properties will be sought in a new line of research just getting underway. A survey of representative knitting mills showed that factors handicapping cotton in knit goods are: (1) high price, (2) inferior yarn uniformity,

(3) excessive linting of yarns during knitting, (4) inability of cotton yarns to withstand the high production speeds of warp knitting, and (5) excessive imports of certain products. A research program has been planned to overcome these deficiencies, and the cotton obtained to initiate the work. Several detailed processing organizations have been developed, and processing will begin.

Chemical treatments for improving the knitability of cotton yarns will also be investigated. This research, which will be conducted under contract by the Philadelphia Textile Institute, was just recently initiated.

2. New and Improved Mechanical Processing Machinery. A carding machine and three versatile and independent auxiliary mechanisms are being developed to improve carding of low-quality cotton. The components can be combined as a carding machine or applied independently to existing machines. The new card is being designed to maximize in one machine the ability to clean, separate, blend, and parallelize cotton fibers, and to remove defects and short fibers. It forms a uniform strand at a high production rate and with a minimum loss of usable fiber. The card consists of two sections and has a unique aerodynamic feed mechanism to reduce yard-to-yard irregularities in the sliver. A separate apparatus removes dust, short fibers, and other defects. The three auxiliary mechanisms will supplement the action of the two-section card in separating, cleaning, and paralleling the fibers. The research will enable manufacturers to produce higher quality products from that part of the cotton crop which is low in quality--the so-called discount cotton.

Two potentially useful techniques for separating cotton into individual fibers at low production rates have been developed. One technique uses a combination of mechanical and aerodynamic forces to individualize the fibers and place them in an airstream created by the system. The second technique utilizes mechanical components to individualize fibers from raw cotton and form them into a thin web. The former apparatus has been used effectively to provide fibers for the alignment and conveying phases of research on electrostatic alignment of airborne cotton fibers.

A recently devised technique and apparatus appear promising for application to the development of a practical unit for electrostatically collecting, transporting, aligning, and forming fibers into a textile strand. The laboratory model apparatus has produced experimental quantities of strands closely resembling standard cotton yarns at rates considerably higher than those of conventional ring spinning methods. Exploratory research with a modification of the apparatus has resulted in the production of short lengths of a unique core constructed yarn. The research suggests the possibility of aligning and mechanically interlacing cotton fibers around any type of core yarn to provide a wide variety of yarn surfaces. This fundamentally new processing technique has demonstrated the feasibility of electrostatically manipulating relatively small quantities of fibers. It has potential as the basis for a new cotton spinning system.

Analysis and field mapping of shaped electric fields by computer techniques has been reduced to practice and is being used to study the conveying of fibers by electric fields. Fiber actions in various arrays of superimposed magnetic and electric fields have been studied by high-speed photography. The ability of cotton to be opened at various temperatures and humidity conditions within selected electric fields is being measured at different levels of temperature and humidity. Significant changes in the amount of force necessary to open fibers as a function of temperatures and humidities indicate that certain atmospheric conditions will facilitate the opening of cotton tufts. Measurement of the charge on cotton fiber in a high intensity electric field has shown values dependent on field intensity, with a mean value of 10^{-8} couombs on a microgram sample of cotton fibers.

Contract research was initiated at Gulf South Research Institute, New Orleans, Louisiana, to explore various approaches for imparting magnetic properties to cotton fibers so that they may be manipulated by electro-magnetic forces to form a textile strand. Methods and apparatus for measuring the magnetic susceptibility of cotton were devised and the apparatus assembled. Basic data on the magnetic susceptibility of various rare earth compounds that could be used to coat cotton fibers were obtained. Two different types of raw cotton (Memphis rain grown and Acala 4-42 irrigated) were measured, and significant differences in the values of magnetic susceptibility were noted. Initial experiments were conducted on adding organometallic compounds and rare earth compounds to the cotton fibers to increase magnetic properties. Some experiments were conducted on creating free radicals in the cellulose molecules in order to obtain magnetic susceptibility. Best results were obtained by using a polyether type polymer to bind small magnetic particles to the cotton fiber and at the same time to insulate them from oxidation. Measurements of the resulting magnetic susceptibility showed that force-to-weight ratios as large as five could be obtained.

3. Durable-Press Cotton Products. The Steam Set process, developed in previous work, appears to be adaptable for use in all general types of commercial steamers. Setting of resins may be properly achieved with low temperature steam if the padded fabric is partially dried prior to steaming. Partial drying of padded fabric is not generally necessary if the resins are set with steam under pressure or with superheated atmospheric steam. Limited evaluations of durable-press cotton garments provided encouraging results.

Accordingly, contract research was recently initiated by United Merchants Research Center, Langley, S. Carolina, to determine the major factors involved in the development of durable-press cotton fabrics on a commercial scale using the Steam Set process. Initial work has been limited to the purchase and preparation of the untreated fabrics required in the plant application studies.

A new approach to circumvent the direct relationship between the reactivity of N-methylol agents and hydrolysis rates of the crosslinked cellulose

under acidic conditions has been discovered. A more durable product from a reactive agent with cellulose is obtained through incorporation of a suitable leaving group (the group that splits out during the crosslinking reaction), such as acetoxy or isopropoxy, to activate the agent. Numerous other leaving groups can be used to achieve similar results, and the approach has also been shown to be applicable to non-nitrogenous systems such as with acetals. A commercial crosslinking agent, Valchem CD 1031, is based on enhanced reactivity using an isopropoxy leaving group. The finish produced by this agent was shown to be more durable than that produced under identical curing conditions with the corresponding conventional reagent. Cooperative work with a chemical company is underway to provide further basic information to commercial firms to help them produce other improved reactants for cotton.

Further development of the technique of aeration of carbamate-sensitized fabrics with moist air has led to the successful use of steaming to release free formaldehyde from the fabric without adverse effects on the properties of the post-cured material. Decomposition of the methylolated carbamate agent during storage of sensitized fabric also could produce free formaldehyde. However, if the fabric is aerated and properly packaged by wrapping in air-impermeable film, there is little generation of free formaldehyde upon prolonged storage. With free access to the air, there is considerably greater decomposition of the agent and subsequent volatilization of the components. An improved method for quantitative formaldehyde analysis has been developed; it is more precise and more accurate than the widely used chromotropic acid method.

In a pilot-plant experiment carried out in a flash ager, the efficacy of steaming has been demonstrated for the removal of free formaldehyde from carbamate-sensitized cotton fabric without adverse effect on the wrinkle- or chlorine-resistance of the fabric upon post-curing. This method of removal of free formaldehyde should make carbamate agents more suitable for use in post-cure durable-press finishing. It is also applicable with other agents that are resistant to hydrolysis. Mild cure finishing with ammonium chloride/phosphoric acid catalysis has been adapted to a post-cure process with the ability to introduce durable creases. Even when neutralizing and washing were omitted from this finishing process, there was no additional loss of strength in the treated fabric during storage. Aluminum chlorhydroxide complex was ineffective as a catalyst in mild cure finishing, but served as a buffer when used in combination with hydrochloric acid catalyst. The result was a finished cotton with a better strength/wrinkle resistance relationship than when hydrochloric acid alone was used as catalyst.

The steam-cure process not only produced improved durable-press fabric in a less cumbersome operation but also yielded fabric with higher strength retention than that from mild-cure and moist-cure processes. Dimensional stability and control of hand were obtained in knitted cotton by using polymeric additives with crosslinking and by mercerization without shrinkage before crosslinking. These methods gave higher bursting strengths

than did use of reactive additives. Knitted cotton receiving mercerization and durable-press treatment retained as much as 90% of its bursting strength. Durable-press post-cure trousers prepared from a knitted cotton had good initial appearance. In knitted cotton, crosslinking primarily prevented strains that cause permanent deformations; in woven cotton, crosslinking did more to increase recovery from these strains. Crosslinking knitted fabrics also reduced growth from repeated strains. Use of hydroxy-substituted carboxylic acids in finishing formulations offset the adverse effect of finishing on soil release.

Certain N-methylol crosslinking agents impart wrinkle resistance to cotton even when applied with alkaline catalysts in place of the usual acidic catalysts. Trimethylolmelamine, N-methylolacrylamide, and dimethylolurea showed this effect, whereas dimethylolethyleneurea and its 4,5-dihydroxy derivative did not. Dimethylolurea was effective at very mild cure temperatures (105-130°C), at which no yellowing occurred in the presence of alkaline catalyst. A phenolic dye was durably bonded to cotton fabric by trimethylolmelamine in the presence of sodium bicarbonate and a softener, to impart 286° dry wrinkle recovery (W+F) along with durable dyeing. Tearing strength retention was 80%. Urea and sulfamide appear to copolymerize and coreact with cotton in the presence of zinc nitrate, and they imparted moderate flame resistance to fabric, as well as durable falso-twist to yarn. When copolymers of ethyl acrylate with N-methylolacrylamide were applied to cotton fabric, delayed curing with acid catalysts imparted moderate wrinkle recovery.

Simultaneous grafting and crosslinking have been performed using crosslinking agents and reactive polyol additives. Fabrics produced with these treatments have improved soil release characteristics as well as the ability to absorb optical brighteners from laundry detergents. This latter characteristic is important in maintaining the whiteness of durable-press garments. The use of alcoholic additives containing acidic or basic groups in conjunction with crosslinking agents has led to the production of durable-press fabrics with such charged groups grafted onto the fabrics. These fabrics can show improved strength, moisture absorption, and abrasion resistance. They also show good absorption characteristics for dyes or optical brighteners opposite in charge to those of the ionic moieties grafted onto the fabric. This approach permits the use of several classes of dyes and optical brighteners not normally useful for cotton. A number of polyol additives have been found effective as agents in fixation systems for the production of durable-press fabrics but improvements in strength or abrasion characteristics have been marginal.

Exploratory work has shown that treating yarns on a textile slasher before weaving is a practical method of improving the properties of durable-press cotton fabrics. Treated yarns can be woven with high efficiency at low relative humidity, a cost saving factor, and the fabrics can be dyed and finished by conventional methods. Directional application of polymer or crosslinking agent can be used to control physical properties of a preferred

yarn system in the finished fabric. Yarns can be sized with a combination of temporary and permanent polymers. The addition of crosslinking agents to this type of size formulation produced fabrics with good durable-press performance and a substantial improvement in fabric strength properties. Studies of combinations of polymer yarn treatments, fabric structures, and improved durable-press finishes showed that fabric weight and weave play an important role in the durability of crosslinked cotton fabrics regardless of prior yarn treatment or fabric finish. Greater yarn mobility and lower fabric weight gave the best resistance to abrasion as measured by the cuff laundry test.

The results of this exploratory research are being used as a guide in a new project to develop warp sizes that avoid stream pollution and produce improved knit and woven durable-press cotton fabrics. The statistical experimental design for the project has been developed, six bales of cotton obtained from commercial sources, and one lot of experimental yarn processed. The 12/1 yarn has been given 18 different polymer treatments, and knitted into fabrics. The knit fabrics will be tested for dimensional stability and the permanence of the polymer film on the yarns.

Contract research was continued at Fabric Research Laboratories, Dedham, Massachusetts, to improve the dimensional stability of all-cotton durable-press fabrics. Based on the results obtained from the 114 different fabric constructions initially produced in the research, the contractor recommended 12 additional constructions. Six constructions of nominal 5.9 ounces/sq.yd. and six of nominal 8.0 ounces/sq.yd. were selected for further evaluation. Fiber blending, yarn manufacturing, and weaving of 15-yard samples of each construction have been completed. Processing was done without difficulty except for spinning. Ends down rate for spinning was considered excessive. Evaluation of the 15-yard samples is now underway. Weaving of 85-yard samples for additional mechanical and chemical treatments is in progress.

Durable-press cotton fabrics with minimal strength loss were prepared by application of methylol triazine and urea-formaldehyde type resins in a low temperature wet-curing process. The triazine was a more efficient type reagent but yellowed on exposure to chlorine bleach. Oven drying followed by extended curing times at ambient temperature was also effective but resulted in greater strength loss. Steam curing gave better strength properties but diminished wrinkle recovery. With urea-formaldehyde and dimethylolpropyleneurea resins, improved efficiency resulted from the use of mixed catalysts such as tartaric acid plus ammonium chloride and citric acid plus magnesium chloride. Curing in superheated steam in a flash ager or oven drying followed by ambient temperature cure were both effective. Additives also enhanced strength, abrasion resistance, and wrinkle recovery properties.

When a jersey fabric knit from commercially mercerized cotton yarn was given durable-press treatments with 7-22% dimethylolethyleneurea (DMEU), it showed little loss in bursting strength (0-12%), whereas the same

fabric construction knit from unmercerized yarn showed large losses (39-46%). When treated with 9% DMEU, then made into trouser cuffs, pressed and cured, the yarn-mercerized fabric had high durable-press ratings (4.5-4.7) and crease retention ratings (4.3-4.9), and also high resistance to laundering abrasion. The cuffs withstood 50 laundering and tumble drying cycles before showing thread breakage, whereas unmercerized cuffs withstood 36 cycles. Both the knit construction and yarn mercerization contribute to increased laundering life. Addition of polyvinyl alcohol to the DMEU formulation decreased shrinkage during laundering to 1.3-1.6% from 3.8-4.9% otherwise obtained without affecting the above performance ratings or laundering life. Remercerization of broadcloth woven of slack mercerized, partially restretched yarn increased both wet wrinkle recovery and laundering abrasion resistance obtained after 9% DMEU treatment. High dry wrinkle recovery and high strength were also obtained.

A cyanoethylation pretreatment before crosslinking improved the strength and abrasion resistance of printcloth and twill fabrics. Cyanoethylated and control twill fabrics treated with a weather-resistant finish are being exposed to determine whether rot resistance imparted by cyanoethylation contributes to weather resistance. Warp compaction increased the warp and filling elongation-at-break, energy-to-break, and flex abrasion resistance of crosslinked twill fabrics. Bursting strength was also improved. It was found that cotton fabric to be rope bleached could be stabilized by a low-level crosslinking pretreatment before rope preparation. Fabric stabilized in this manner was substantially more resistant to the formation of rope marks than was untreated fabric. The crosslinks formed when cotton was treated with conventional nitrogenous crosslinking agents were easily hydrolyzed by steaming under pressure, even in the absence of a catalyst. The physical properties of steam-hydrolyzed fabric were almost identical to those of an acid-hydrolyzed control.

In contract research conducted by Auburn Research Foundation, Auburn, Alabama, a combination of mechanical and chemical treatments was used to improve durable-press cotton fabric. Mechanical compaction changed the structure of cotton broadcloth in a way different from that obtained in weaving. Yarn density was increased by crimp induced during compaction. Alternatively, fabrics were stretched to give changes in construction. Polyurethane was used to stabilize either compacted or stretched dimensions of fabric after mechanical treatment and before crosslinking treatments. Cotton twill fabric so treated had 30% higher tensile strength and withstood 50% more laundering than a counterpart given a conventional pad-dry-cure crosslinking treatment. Slack mercerization was also utilized as a pretreating process to modify fabric construction and impart greater warp crimp in a subsequently crosslinked cotton twill fabric. This pretreatment followed by warp compaction of the sensitized fabric gave an increase, after curing, of tensile strength (20%), tearing strength (25%), and wear life of laundered cuffs (50%) over that obtained from conventionally crosslinked samples.

The cooperative research study with the Cotton Producers Institute to determine the role of fabric structure in the durable-press performance of all-cotton fabrics is well underway with the weaving of 242 of the 400 experimental fabrics planned. One hundred sixty of the woven fabrics have been given a conventional durable-press finish and are now undergoing tests to determine their physical properties. Data from these tests are just beginning to accumulate. Efficient weaving practices required that the fabrics be woven in the order of decreasing warp thread count, which resulted in a seemingly random order of fabric preparation. Consequently, although more than half of the fabrics have already been woven, the data are not yet complete enough to permit even subgroup analyses. Test trouser cuffs have been fabricated from the DP-treated fabrics; these will soon be subjected to repeated laundering to determine their performance in washing and tumble-drying. Meanwhile, preparation, finishing, and evaluation of the remaining fabrics continue. One-yard samples of all the fabrics have been catalogued and filed as part of a fabric library being established for reference purposes.

In cooperative work with the Cotton Producers Institute to develop improved cotton fabrics for durable-press work trousers, a total of 80 experimental fabric structures in the nominal 8.0 to 8.5 oz./sq.yd. weight range have been woven and finished. The fabrics were given three different durable-press treatments, including a conventional resin finish and two experimental finishes. Evaluation of the fabrics treated with the conventional finish has been completed. Results indicate that resistance to edge abrasion as measured by home laundering techniques can be improved by simultaneously increasing ends and decreasing picks per inch, and by using a coarser filling yarn. Overall, 3/2 45° twill weave fabrics performed best in the laundering tests. Variations in filling yarn twist had no appreciable effect on edge abrasion or strength properties. The breaking and tearing strengths of the treated fabrics were sufficient in most cases to meet industry minimum specifications for work trouser type fabrics.

A vapor phase system for crosslinking cotton with formaldehyde was investigated further. This closed, constant pressure, cell type system utilizes a container of expandable plastic film that encloses the cotton textile and the reagents which are spread over a matrix having a large surface area. Although additional information relative to optimizing reaction parameters and product properties was obtained, the properties were not significantly better than those produced by conventional crosslinking with other agents. However, the basic information should be applicable to vapor phase graft and in situ polymerizations being investigated under a new project.

4. Weather-Resistant Cotton Fabrics. In continued cooperative research with the Canvas Products Association International and the Cotton Producers Institute, phenylmercury-zirconium finishes, with and without durable-press treatments, have been developed through the pilot-plant stage and applied to cotton sheeting and toweling. Biocidal activity was retained by these

fabrics through ten simulated launderings equivalent to 50 commercial launderings. A process for orange to brown fungicidal mineral dyeings from single-bath systems has been developed through the laboratory stage and is ready for pilot-plant application. Ammonium salts have been substituted for sodium salts in the Zirchrome Process. These give deeper chrome green color shades and reduce the problems of rewetting. A commercial firm has evaluated the process and plans to market it. Two companies have been issued licenses on patents covering Zirchrome mineral dyeing and phenylmercury-zirconium biocides.

The process using premercerization, superheated steam curing, and compaction produced best tearing strength properties in resin-finished Osnaburg for sandbags. Addition of urea and/or N-methylol resins reduced fabric tendering in mineral dyeing and improved rot resistance. The role of air pollution in fabric degradation is being studied with the N.Y. State Board of Health. A new method of aqueous application of zinc oxide produced light- and mildew-resistant cotton. Selected laboratory and commercial flame-retardant finishes, durable to repeated washing-tumble drying, degraded when exposed to weather, sunlight, heat, and line drying. Hydroxymethyl phosphonium hydroxide (THPOH)-ammonia (NH_3) and commercial finishes were most affected by sunlight. Application of either a blue or colorless (white) pigment improved resistance to actinic degradation. Degradation on thermal exposure was severest for the phosphonate and THPOH- NH_3 type finishes. Overall, the hydroxymethyl phosphonium chloride (THPC)-amide and the aziridinyl phosphine oxide (APO)-THPC finishes were most resistant to light and heat. Changes noted in the THPC-amide finish appear to be due to the urea component.

Contract research to develop improved coated cotton fabrics with optimum strength-weight characteristics for outdoor uses was continued at Fabric Research Laboratories, Inc., Dedham, Massachusetts. A more extensive and detailed verification of possibilities of minimizing losses in tearing strength was carried out. The following procedures were investigated: (1) application of a soft base coat topped with a harder surface coat, and (2) filling the pores of the fabric with a water-soluble material prior to coating. Final evaluation of the results is in progress.

5. Soil-Resistant Cotton Textiles. Cotton fabrics treated with 1.5% 1-ethoxymethyl-3-(1,1-dihydroperfluorooctyl)-urea possessed high oil repellency, good durability to laundering, and good soil release properties (except for dirty motor oil). In contrast to reports that commercial fluorocarbon finishes cause large strength losses when treated fabrics are weathered, fabrics treated with the urea finish retained even more strength than the untreated control. This may indicate a higher degree of stability to actinic degradation for the urea finish. Although the finish based on tetrakis(hydroxymethyl)phosphonium chloride and 1,1-dihydroperfluorooctylamine imparts high oil repellency and good soil release to cotton, its durability to laundering was not satisfactory when the ammonia cure was used. Laundering durability was improved by using hexamine as an additive and a high-temperature cure. In a study of basic additives, best overall

results were obtained when sodium acetate was used to raise the emulsion pH to 5-5.5. In a spectroscopic study related to the above finish, it was found that with certain amines, the presence of formaldehyde is not required for reaction to occur with tris(hydroxymethyl)phosphine (THP).

6. Insect-Resistant Cotton Bags. Research on insect-resistant treated (IRT) cotton bags was continued in cooperation with the Stored-Product Insects Research and Development Laboratory at Savannah, Georgia, the Textile Bag Manufacturers Association, and the Agricultural Stabilization and Conservation Service. The observation that migration of insect repellent from IRT cotton into stored foods was directly proportional to oil content and inversely proportional to particle size of the foods indicated that migration was by a solid solution transfer mechanism rather than by vaporization and readsorption. Therefore, barriers such as polyvinyl chloride (PVC) between IRT-fabric and foods should be more effective than formulation additives in retaining insecticide on fabric and in reducing contamination of food. In a 6-months' overseas storage test, IRT laminated cotton bags without seam holes (tape over stitches closures) showed effective insect resistance; however, present insect-resistant bags are not strong enough to resist excessive damage during handling. Large-scale static food storage tests are planned with stronger, IRT laminated cotton bags without seam holes (tape over stitches closures and woven cotton bags) that have paper ~~or~~ PVC liners. Laminated IRT-paper/paper/woven cotton bags, IRT-woven cotton bags with PVC liners, and conventionally sewn IRT-cotton bags with PVC inserts were developed and fabricated for inclusion with IRT laminated cotton/paper bags in the large-scale food storage test now being arranged.

SELECTION AND CARE OF CLOTHING AND HOUSEHOLD TEXTILES

A. Chemical and Physical Investigations to Improve Products

1. Better Fitting Consumer Apparel. The contractor (Boston University, Boston, Massachusetts) has continued research to obtain data on body dimensions needed in the development of satisfactory systems for sizing apparel for elderly women. Further tabulations of the data have been made. For example, the measurements for ages 65-69 have been compared with comparable measurements for ages 70-79. Very little difference is visible between these two age groupings, thus allowing for emphasis on the total series ages 65-79 combined. Correlation values between the various measurements have also been computed, with a whole series of partial correlations with other key measures being held constant. The results of the computer output are now being put into tabular form. Cumulative percentages are being calculated and frequency distributions are being collated for all the measurements.

2. Improved Techniques for Consumer Care of Textiles. In completed contract research at the Southern Research Institute, Birmingham, Alabama, it was determined that fabric type was a significant factor in the rate of vaccinia virus reduction brought about by the laboratory laundering process, with

the least virus titer reduction seen on woolen fabrics. Water temperatures of 130-140°F in the absence of detergent were effective against vaccinia virus; lower temperatures were not significantly effective. Machine drying of the laundered vaccinia virus-contaminated fabrics markedly lowered the amount of remaining virus on all fabrics tested. Research has not been conducted to determine whether such survival and transfer will occur in service.

Contract research was initiated at Southern Research Institute, Birmingham, Alabama, to determine the extent of survival and redeposition of viruses during drycleaning of textiles. The standard laboratory drycleaning process caused a reduction of virus titer on all fabrics, but viruses were demonstrated in many instances to persist through the process to be transferred from contaminated fabrics to uncontaminated fabrics during drycleaning. There was a greater retention of viruses on the wool-containing fabrics than on any other types of fabric. A reduction of virus was observed when virus was placed on fabrics treated with durable-press finishes, which indicated that such finishes have virucidal properties. The commercial, coin-operated, automatic machine drycleaning process has been found to be superior to the standard laboratory drycleaning process, since polio virus could not be detected on wool blanketeting, cotton sheeting, or durable-press finished fabrics after drycleaning. In addition, transfer of polio virus to sterile fabrics during the automatic drycleaning process could not be demonstrated.

An investigation of the effect of laundering variables on edge abrasion in garments made from durable-press fabrics is being conducted in contract research at the University of California, Davis, California. The men's durable-press trousers currently being studied are at the 18th cycle of wear and laundering. The garments are being routinely evaluated by assignment of a wear score and rating for edge abrasion by comparison with a photographic standard. For the laboratory launderings, sample cuffs of four different fabrics have been constructed. These cuffs are being laundered by the normal wash-dry procedure, with and without each of the following modifications: cuffs turned wrong side out, drying time extended 10 minutes, wash time shortened to 8 minutes, wash and rinse temperature 80°F, slow agitation speed in wash cycle, nonionic detergent in wash, fabric softener added to rinse, sodium hypochlorite added to wash water, enzyme pre-soak preceding wash.

Other research is concerned with the correlation of wear tests with laboratory tests of experimental and standard weave cotton fabrics. About 210 pairs of trousers were constructed to evaluate durable-press characteristics of: (a) a fabric construction developed at SU; (b) steam-set finishes; and (c) a standard commercial control fabric. Wear studies and laboratory testing of trousers and dummy cuffs are underway.

REDUCTION IN HEALTH HAZARDS INVOLVED IN USE OF TEXTILES

A. Chemical and Physical Investigations to Improve Products

1. Synthesis of Compounds Potentially Useful for Imparting Flame Retardancy to Cotton. In P.L. 480 research at the Hebrew University of Jerusalem,

Israel, eight new alkylenebis(dichlorothiophosphamides) were synthesized and reacted with aziridine to produce the corresponding new alkylenebis[P,P-bis(1-aziridinyl)-thiophosphamides]. Infrared absorption spectra, nuclear magnetic resonance spectra, and alkylating activity of the aziridines were determined. The rate of opening of the aziridine ring as a function of other substituents decreased in the order P-C>P-N>P-O; steric factors also affected the rate. If, as indicated, only one aziridinyl group per molecule undergoes the alkylating reaction, the crosslinking of cotton cellulose may not be possible. This information may be useful in screening the aziridines as flameproofing and crosslinking agents for cotton cellulose.

2. Alteration in Physical Properties of Cotton by Flame-Retardant Treatments. Research has been initiated to determine changes in physical properties of cotton fibers and fabrics that result from flame-retardant treatments and to relate these changes to processing variables. Cottons have been treated by several processes for imparting flame retardancy, and fiber and fabric properties are being measured. Knowing the mechanisms through which the physical properties are altered should aid in devising processes to produce improved flame-retardant cotton textiles.

B. Technology--Process and Product Development

1. Flame-Retardant Cotton Textiles with Other Desirable Properties. Systematic studies to determine the relative value of tetrakis(hydroxymethyl) phosphonium chloride (THPC) and tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH) in flame-retardant processes were conducted by treating cotton fabric with THPC-THPOH formulations in which the mole fraction of THPOH was varied from 0.02 up to 0.98. Heat-cure, steam-cure, and ammonia-cure techniques were used to fix the flame retardants in the fiber. Changing the proportions of THPOH/THPC in flame-retardant formulations had little effect on add-on of retardant, char length, and moisture regain of treated fabric but did have significant effects on most other fabric properties, including breaking and tearing strengths and durability of the finish. The method of curing had significant effects on wrinkle recovery, stiffness, and strength retention of treated fabrics. A mole fraction of THPOH close to 1 was shown to produce flame-retardant fabrics with best overall properties. In experiments to determine the importance of the source of nitrogen in phosphorus-nitrogen flame retardants for cotton, it was found that nitrile nitrogen is a liability in the flame-retardant system, whereas amine or amide nitrogen is helpful.

A flame retardant that is stable to repeated laundering has been developed for cotton fabric; it is based on the trimethylol derivatives of tris(carbamoylethyl)phosphine oxide. In a study of the mechanism of the reaction of THPOH, it was found that the presence of free formaldehyde is necessary for polymerization to occur between tris(hydroxymethyl)phosphine (THP) and some amines. Cotton fabric treated with several flame retardants

based on THPC lost its flame retardancy at a more rapid rate when a chlorine bleach was used during laundering. A new reaction in THPC chemistry was discovered: THPC reacts with tributyl phosphine to give a new compound, thereby leading to a better understanding of the chemistry of this important flame retardant.

Cooperative research with the U.S. Army Natick Laboratories, Natick, Massachusetts, to impart flame and rot resistance to cotton was continued. Sateen was treated with THPOH-thioethyltriphenyllead emulsions and then ammonia cured to impart flame resistance; after 15 months' weathering, it had less mold growth and slightly higher breaking strength than the control. Similar weathering results were obtained for fabric treated with THPOH-NH₃ flame retardant and then with a thioethyltriphenyllead solution. After 4 weeks of soil burial, printcloth treated first with a 5% thioethyltriphenyl-lead solution and then with 30% THPOH-NH₃ retained 35% of its original breaking strength. Cotton fabric treated with a cyanamide-THPC-phosphoric acid (H₃PO₄) formulation had durable flame resistance and wrinkle resistance. Wash-wear rating for the THPC-cyanamide-H₃PO₄ treated fabric initially ranged from 3.5-3.7 and after 30 launderings was 3.0. The treatment is suitable for a delayed-cure process and imparts little color when bleached. To increase the strength of the treated fabric, the pH of the THPC solution was varied from 1.2 to 8.0. The strength of the treated fabric increased as the pH increased, but the durability of the finish decreased after the pH increased above 6.

New chemical systems to impart improved flame resistance and safety to cotton textiles are being investigated in other cooperative work with the U.S. Army Natick Labs. Organic compounds (such as chloromethylphosphonic acid and propylammonium phosphate) and inorganic compounds (such as dibasic ammonium phosphate, zinc nitrate, ammonium sulfonate, sodium ammonium phosphate, magnesium chloride, copper chloride, sodium sulfate, sodium perborate, and mono-, di-, and tribasic sodium phosphate) were substituted for phosphoric acid in the THPC-cyanamide formulation to improve the strength of the treated cotton fabric. Only ammonium phosphate, sodium ammonium phosphate, and the di- and tribasic sodium phosphate incorporated in the treating solution imparted durable flame resistance to the fabric. Di- or tribasic sodium phosphate substituted for phosphoric acid in the treating bath imparted flame resistance to the fabric for over 30 launderings and increased its breaking strength 30% and tearing strength 35% in comparison with those of the fabric treated with the acid formulation.

Work was initiated to develop flame-resistant finishes for cotton fabric that are durable to laundering after sunlight exposure or line drying. Experiments in which high halogen content fire-retardant formulations were applied at varied pickup levels to cotton fabric from solution and dispersion systems are in progress. Applications of latex dispersions are also planned. The flame-resistant finishes will be evaluated for durability to laundering and to sunlight exposure. Fire-retardant formulations resulting in finishes with improved durability, particularly at low add-ons, to laundering, actinic and thermal exposures will be investigated.

Pressure-vacuum pilot plant and bench scale reactors have been installed for use in research on vapor-phase reactions to impart flame retardance and other special properties to cotton textiles. Auxiliary hardware, instrumentation, controls, and services are being connected. Initial research will involve studies of the use of high pressure ammonia gas as a curing agent for the THPOH-trimethylolmelamine flame-retardant finish under development at SU. A literature search is underway to uncover other reactants that could be used to impart flame retardance after application from a vapor phase system to yield either crosslinked or in situ polymerized species within or on the cotton.

2. Flame-Retardant Cotton Batting. Research to develop efficient low-cost flame-retardant treatments for cotton batting was continued in cooperation with the National Cotton Batting Institute, the Textile Fibers and Byproducts Association, the National Cottonseed Products Association, the Foundation for Cotton Research and Education, and the National Association of Bedding Manufacturers. The feasibility of impregnating cotton batting rawstock (1st cut linters and textile wastes) with semidurable flame retardants before mechanical processing has been demonstrated. The projected cost of such treatments is about 3.5 cents per pound, including amortization of equipment over a 5-year period. Urea phosphates, borated amido polyphosphates, propyl ammonium phosphates and phosphorylated derivatives of dicyandiamide all yielded acceptably flame-retardant products at add-ons of 10% or less. The addition of nitrogenous resins to the treating formulations enhanced both the flame retardance and the resilience of the products. Fiber breakage during subsequent garnetting was minimized by adding a textile type of softener to the treating formulation. The cotton batting industry is following this development with keen interest, and at least one company is planning to install the process on a pilot basis.

ABATEMENT OF POLLUTION

A. Technology--Process and Product Development

1. Reduction of Stream and Air Pollution That May Result from the Processing of Cotton Textiles. As noted earlier in this report, research was recently initiated to develop warp sizes that avoid stream pollution and produce improved durable-press cotton fabrics. A series of knit fabrics produced from yarns given different polymer treatments is currently under evaluation. A conference was held with officials of the Department of Interior, Water Pollution Control Division, on water pollution problems due to textile processing. Technical literature and test methods were also obtained to aid in guiding this research.

Research is also being conducted to develop nonaqueous scouring and mercerizing processes to improve fabric properties and reduce stream pollution. In previous work, a two-way stretch, crosslinked fabric with balanced stretch, good recovery properties, and improved wear life was

produced by a combination of slack mercerization and compaction treatments. A study is in progress to determine optimum fabric constructions for warp compaction. The fabrics vary in weave, warp and filling thread count, and filling yarn construction. The fabrics have been desized, scoured, boiled-off, bleached, crosslinked, compacted, and then cured. Bleaching removed more noncellulosic constituents from greige fabric than did solvent extraction and desizing. Liquid ammonia proved to be a very efficient mercerizing agent for cotton. Although it does not swell cellulose as much as aqueous sodium hydroxide, it causes an increase in tenacity comparable to normal mercerization in a fraction of the time. Tension mercerization of rope bleached fabric with either sodium hydroxide or anhydrous ammonia greatly reduced, and in many cases removed, the rope marks present in such fabric. Treatment of dry cotton yarn with liquid ammonia, followed by immersion of the complex formed into either acetone or tetrahydrofuran, resulted in the strong conversion of cellulose I to cellulose III.

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NEW AND IMPROVED TEXTILE PRODUCTS

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COTTONSEED

Problems and Objectives

Cottonseed products face increasing competition for markets: edible products from the oil must compete with those from other vegetable oils and animal fats, and the meal--now used chiefly as a protein supplement in feeds for ruminants--is being supplanted by synthetic urea and other sources of nitrogen. To retain these markets and to open new ones is the goal of utilization research on cottonseed. Food products must be developed to improve the competitive position of cottonseed oil and meal, to provide inexpensive protein concentrates for domestic low-income groups, and to help alleviate the worldwide protein shortage. There is also need to improve the quality and nutritive value of meal used for feeds. However, the wholesomeness of both food and feed products must be assured by controlling various undesirable natural or adventitious components. Finally, to extend cottonseed's markets beyond food and feed, research is needed to derive industrially useful products.

Specific objectives of the research are:

1. To improve processing methods to preserve or enhance the intrinsic desirable qualities of the oil and meal.
2. To develop new and improved food, feed, and industrial products.
3. To expand domestic and foreign markets for cottonseed products by tailoring them to meet consumer preferences.
4. To insure the safety and wholesomeness of cottonseed products used for food or feed.

Progress

NEW AND IMPROVED FOOD PRODUCTS

A. Chemical Composition and Physical Properties

1. Properties of the Triglycerides. P.L. 480 research at the University of Bombay in India is directed toward determining the properties of pure saturated di- and triacid triglycerides of cottonseed oil. Additional quantities of fatty acids, 1-monoglycerides, 1,3-diglycerides, and triglycerides were prepared. The density, viscosity, and refractive index of seven series of triglycerides were determined over appropriate temperature intervals. Pancreatic lipase hydrolysis was used to determine the extent of acyl migration, if any, during the acylation. The starting materials used for the synthesis--1-monoglycerides or 1,3-diglycerides--were determined to be pure. A few of the triglycerides found to be contaminated by this acyl migration are being resynthesized.

2. Properties of the Proteins. A method was devised to prepare 70% protein concentrates from defatted oilseeds (glandless cottonseed, sunflower, peanut, soy) by aqueous extraction at neutral pH. Sugars, color, protein, and flavor components were removed, leaving intact protein bodies, which were stabilized by calcium, and cell wall fragments. The product should differ from other 70% concentrates in functionality and flavor. The low and high molecular weight protein isolates of cottonseed were prepared by selective precipitation (S/P) rather than selective extraction (S/E). S/P reduces the number of centrifugation steps and gives comparable yields but different solubility characteristics. Functional evaluation showed that the low molecular weight isolate (S/E) had an unusual foam capacity and stability at acid pH. Washing of the isolate at pH 4.8 before drying eliminated heat coagulability. Glandless cottonseed flour, air-classified concentrate, and high molecular weight isolate were substituted for flour in a bread formulation at 3% and 10% levels. The protein quality of bread with each cottonseed product at 3% was equal to that of bread with 3% non-fat dry milk. At the 10% level, protein quality equaled that of bread with 3% soy flour (60% protein). This research was partially supported by the Foundation for Cotton Research and Education, the National Cottonseed Products Association, and the Cotton Producers Institute.

The findings reported above are being extended in new research sponsored in part by the same cooperators. Isolates were prepared from liquid cyclone flour by selective extraction and selective precipitation procedures. Yields of the major, acid-soluble, storage protein isolate were comparable to those from glandless flours. The storage proteins formed insoluble complexes with the calcium ion under alkaline and acid conditions. Cottonseed isolates can now be prepared by six different procedures. The effect of concentration, pH, and temperature on the consistency of slurries of glandless flours and concentrates was determined. Consistency increased with concentration. Cell wall constituents produced a pudding-like consistency, which increased with concentration, pH, temperature, and cooling. Effects at acid pH were negligible. Protein bodies remained intact at neutral and acid pH and aggregated to small beads at approximately 80°C. At alkaline pH, protein bodies ruptured and at 80°C the hydrated proteins coagulated.

Morphology of particles in samples collected during the processing of glanded cottonseed with the liquid cyclone process was examined by light and electron microscopy: gossypol glands; pieces of whole tissue with and without adhering glands; aleurone grains; and small, morphologically unidentified structures that probably correspond to cell wall fragments and interspherosomal cytoplasm. Distribution of these particles in the fractions showed that the liquid cyclone thoroughly removes glands from other fractions but the liquid cyclone underflow should be recycled through the whole process; the doxies are not useful for particle separation.

Recently initiated research is designed to investigate techniques for simultaneously extracting oil and protein from cottonseed by the use of aqueous media. In preliminary research to provide background information,

spherosomes, the intracellular storage sites of oil, were isolated on a large scale from oilseeds and leafy plant materials. Regardless of the plant source, spherosomes appeared similar with respect to size, morphology, and staining characteristics. However, spherosomes isolated from leafy materials were composed of 80% lipid, 40% protein, and 0.2% phospholipid, whereas spherosomes from oilseeds contained 99% lipid, 0.4% protein, and 0.2% phospholipid.

3. Reactions of Gossypol. In contract research at Savannah State College in Georgia, gossypol was shown to undergo interesterification reactions with methyl esters of long-chain fatty acids, such as stearic, to yield amorphous esters insoluble in hexane, alkali, or water. Evidence from infrared spectra, elemental analysis, saponification equivalent, and model reactions indicated that the transesterification product with stearic acid was a gossypol distearate with the fatty acid esterified at the 6,6' hydroxyl positions of the gossypol molecule rather than at the 7,7' positions. Analogous reactions undoubtedly occur between gossypol and the glyceride esters of cottonseed oil to yield alkali-insoluble chromogens.

B. Technology--Process and Product Development

1. New and Improved Products from the Oil. A study of the parameters of the new process for preparing sucrose esters of fatty acids showed that it can yield only mono- through tetraesters. These esters have utility as food and cosmetic emulsifiers and as biodegradable detergents. Fatty acid esters of sucrose-adipic acid polymers were prepared as a series of new products that may have commercial value. For example, sucrose tetra-linoleate condensed with adipic acid compounds resulted in a superior drying oil. As the first step in the purification method developed, unreacted sucrose was removed by extracting the crude esters with hexane. Subsequent filtration through a micropore membrane separated the sucrose esters from the glycerides and free fatty acids but only partially removed the soaps, which may have formed a complex with the sucrose esters.

A novel hydrogenation catalyst useful in making cocoa butter-like fats was developed by adsorbing submicroscopic particles of platinum or palladium on precipitated nylon. Additional solvents were found suitable for preparing this catalyst, although each required an exclusive procedure. The geometrical isomerization of linoleins has promise in producing the higher-melting products. When oxides of nitrogen were used as catalysts, yields were unpredictable: 75 percent of theoretical or less. Selenium catalyst gave higher yields, but still less than theoretical. Fractional crystallization of the products from a solvent did not concentrate the trans isomers to yield good cocoa butter-like fractions, as desired. Primarily monosaturated triglycerides were separated from the disaturated. The stearine from solvent-winterized cottonseed oil was fractionally crystallized from solvent to give nearly pure 1,3-dipalmito-2-unsaturated triglycerides, which melted over the narrow range of 23 to 29°C. This fraction

was isomerized with selenium and then tempered to increase the melting range to 30 to 44°C, the range for confectionery fats. Tempering was slow, requiring several weeks at 25°C.

2. Other Edible Products. Plans are underway to install a versatile pilot plant designed for the sanitary production of 50 pounds of edible cottonseed protein isolates per day. Specifications have been submitted for equipment, including centrifuges, spray dryer, pasteurizer, agitators, pumps, and tanks. A trial commercial run to process glandless cottonseed produced an edible high-protein (56%) cottonseed flour that had light color and high protein solubility, and was amenable to air classification. However, the inclusion of hulls and fine meats lowered the acceptability of the product, which contained small hull particles and had high microbiological population. Process modifications are being studied to eliminate these problems. A jet pulverizer air classifier and accessory equipment have been installed for preparation of cottonseed protein concentrates, and the equipment is being tested.

The pilot plant for the liquid cyclone process was operated on a semi-continuous basis through five runs, yielding 1,700 pounds of an excellent cottonseed flour, which was bland and very light creamy yellow. Its approximate composition was 0.02% free and 0.06% total gossypol, 1.0% oil, 68.9% protein, 99.5% nitrogen solubility, 3.96 grams EAF lysine per 16 grams nitrogen, and 40 ppm of residual hexane. Commercial evaluations of samples from 1 to 100 pounds for acceptability in food and beverage formulations and as a source for protein isolates produced encouraging results. The process is being evaluated on a pilot-plant scale at the Sundatta Oil Mill, Hubli, India, under the direction of Dorr-Oliver, Inc. A simple and efficient volatilization technique requiring little operator time was developed for quantitatively determining parts per million of residual hexane and isopropanol in oilseed meals and flours.

NEW AND IMPROVED FEED AND INDUSTRIAL PRODUCTS

A. Chemical Composition and Physical Properties

1. Improved Cottonseed Meal for Feeding to Nonruminants. Optically active gossypol was found in all samples of cottonseed obtained from California, Texas, and Mississippi. Improved isolation procedures resulted in obtaining dextrorotatory (+) gossypol (as the dianilino derivative) having optical activity about 40 to 50% of the theoretical value instead of a previously reported 4 to 7%. Attempts to resolve racemic (\pm) gossypol by chemical methods have not yet been successful, nor has elution of (\pm) gossypol from optically active adsorbents produced gossypol of significant optical activity. (+) Gossypol may be boiled in toluene for an hour at 116°C without loss of optical activity. However, it lost 40% of its optical activity upon heating for 10 minutes in ethylene glycol at 180°C. There are indications that optically active gossypol may play an important role in the resistance

of certain Gossypium species to insects. This relationship will be determined when sufficient amounts of optically active gossypol of reasonable optical purity become available.

Gossypol toxicity has hindered the full utilization of presently available commercial cottonseed meals in the diets of small animals. Since chelation with metals appears to be a promising means of deactivating gossypol, investigations were conducted to provide simple and effective methods of preparing gossypol complexes and measuring their spectroscopic, magnetic, and other important properties. A thorough investigation of the physical-chemical properties of gossypol complexes revealed the mode of bonding and spectroscopic properties. A simple test to determine chelate formation was proposed, and sufficient evidence was obtained by electroanalytical and spectroscopic techniques to establish possible structures and mode of bonding of the complexes. The results of this basic research have contributed to the background information needed to improve the nutritional value and utility of cottonseed meal.

In a P.L. 480 project at the University of Madras, India, scientists are obtaining basic data essential in the design of rectification columns to recover hexane-acetone-water solvent in oilseed extraction processes. Isobaric vapor-liquid equilibrium data were obtained experimentally for the partially miscible binary system n-hexane-water, the miscible binary systems acetone-water and acetone-n-hexane, and the partially miscible ternary system hexane-acetone-water. Compositions obtained from the experimental data were in good agreement with those predicted from the Redlich-Kister equation as modified by Nagata. Addition of refined cottonseed oil to the acetone-hexane binary system resulted in strong shifts of vapor-liquid equilibria and azeotropic compositions toward more ideal behavior. This study is now being extended to the ternary system. Liquid-liquid equilibrium relationships for the ternary heterogeneous n-hexane-acetone-water system at three temperatures (25° , 30° , and 35°C) were also determined experimentally. Heat of mixing values for the endothermic reactions involved were measured in a suitable calorimeter.

2. Derivatives of Fatty Acids Potentially Useful to Industry. In research conducted to determine the structure and properties of cottonseed fatty acid derivatives from spectral data, highly pure esters were prepared from a number of commonly occurring mono- and dienoic acids. Polymorphic modifications were investigated on the basis of heating and cooling curves. Infrared spectra and x-ray diffraction patterns were obtained on the different polymorphs at temperatures to -195°C . Wide line nuclear magnetic resonance spectra were also obtained on some of the higher melting compounds. These results and the procedures and techniques devised should have significant importance in further investigations of the physical and chemical properties of this important group of compounds, with the ultimate objective of providing useful products from cottonseed fatty acids.

At the Indian Institute of Science, Bangalore, India, P.L. 480 research is continuing on the chemical transformation of saturated fatty derivatives from cottonseed oil. Thermal isomerization of organoboranes prepared from alpha,beta-olefins (1,1-diphenyl-1-propene, -1-butene, -1-hexadecene and -1-octadecene) was investigated as a route to synthetic preparation of alpha,omega-difunctional compounds from the saturated fatty acid derivatives. The reaction mixture from hydroboration, contrathermodynamic isomerization, and oxidation treatments of 1,1-diphenyl-1-propene was separated; the desired products (3,3-diphenylpropanol and its 3,5-dinitrobenzoate derivative) were characterized by gas and thin-layer chromatography. A mixture similarly prepared from the butene contained the desired 1,1-diphenylbutanol, identified by gas chromatography. The reaction mixtures from the hexadecene and octadecene are still under investigation.

B. Microbiology and Toxicology

1. Effects of Gossypol in Feed. The digestion and metabolism of gossypol in cottonseed meal are being studied in contract research conducted by the Texas Agricultural Experiment Station at College Station. ^{14}C formyl labeled gossypol orally administered to pigs was rapidly excreted in the feces--more than 95% in 20 days. The major pathway for excretion was via the bile into the intestines; decarbonylation of gossypol to CO_2 and apo-gossypol was a minor route, accounting for only 2% of the dosage. The decrease of gossypol in the tissues from 33% after one day to 1% after twenty days indicated essentially complete depletion after rations containing gossypol were withdrawn. The metabolic pathway for eliminating dietary gossypol in the pig seems to be similar to that previously found for rats and laying hens.

Related research is being conducted at the "Mario Negri" Pharmacological Institute, Milan, Italy, in a P.L. 480 project. Acute toxicity to gossypol as measured by the LD_{50} was determined for four species of animals: the guinea pig was most susceptible, followed by the rat, mouse, and chicken. Gossypol administered by intraperitoneal injection was much more toxic than by intravenous or oral routes. Subacute levels of gossypol administered orally to rats evoked an increase in the weight of liver, spleen, and--to a greater degree--intestine. The amino acids L-lysine and L-arginine and serum albumin had no effect on the intestinal hypertrophy induced by gossypol, but aluminum hydroxide, sodium hydrosulfite, iron choline citrate, and ferrous sulfate all had a pronounced protective effect. Oral administration of gossypol to rats produced significant decreases in the plasma iron as long as four hours after administration, but the levels returned to normal in twenty-four hours. Ferrous sulfate administered with gossypol was very effective for preventing the lowering of plasma iron. Thin-layer and gas-liquid chromatography indicated that only bound forms of gossypol were present in the urine and in the organs of rats after oral ingestion of gossypol.

C. Technology--Process and Product Development

1. New Products Suitable for Industrial Use. The following amides were evaluated as lubricants: the N,N-dimethyl, -dipropyl, -dihexyl, -dimethylbutyl, -dimethoxyethyl, -diethoxyethyloleamides; the N-methoxyethyl, -methoxyisopropyl, -ethoxyethoxypropyl, -ethoxyethoxyethoxypropyleamide; the N,N-dibutyl derivative of the 9,10-epithio, 9,10-12,13-diepithio, and 9,10-12,13-dichlorostearamides; and N-(9,10-epithiostearoyl)-morpholine. As base lubricants, many of these amides gave lower wear scars than did paraffin oil or di-2-ethylhexylsebacate (DOS). The N- and N,N-alkoxyalkyloleamides were particularly good, performing better than Aero Shell Mil L-7808 (DOS + additives). The epithio and diepithiostearamides exhibited excellent extreme pressure lubricant characteristics, both as base lubricants and as additives for diesters and other amides; they were superior to SAE No. 90 commercial hypoid fluid. Manufacturing costs based on a range of chemical prices were estimated for N,N-dibutyloleamide, N,N-dimethyloleamide, and N-methyl-N-(2-oleoyloxyethyl)oleamide at annual production to 50 million pounds: the costs were 13.8 to 32.6, 13.9 to 25.3, and 13.9 to 26.4 cents per pound, respectively.

PROTECTION FROM POTENTIALLY HARMFUL MICROORGANISMS, TOXINS, AND NATURAL CONSTITUENTS

A. Microbiology and Toxicology

1. Reactions and Effects of Cyclopropenoids. In research conducted under a grant to Boston University in Massachusetts, procedures were previously developed for the synthesis of methyl sterculate, methyl malvalate, and labeled methyl malvalate with the radioactivity in the methylene carbon of the cyclopropenoid moiety. Based on these results, multi-step procedures were developed for the practical synthesis of additional isomers of labeled methyl malvalate with labeled ^{14}C at the 1-position, at the 9-position, and at the 10-position of the molecule. These practical techniques represent the first successful synthesis of these extremely valuable compounds. Several grams of these labeled isomers have been provided to WU for biological investigations designed to help elucidate the metabolic fate of malvalic acid, the principal cyclopropenoid in cottonseed oil. These investigations should help to determine whether the cyclopropenoids in cottonseed oil impart adverse physiological effects.

To develop information on the destruction of the physiologically active cyclopropene acids (malvalic and sterculic) found in cottonseed oil, the reaction of palmitic acid with methyl sterculate was investigated. Moderate heating caused the formation of several compounds whose structures have been tentatively identified and whose properties are being investigated. Attempts to destroy cyclopropenes by an electrolytic reduction and by treatment with lipoxidase were unsuccessful. Physical properties of the methyl esters of the cyclopropene and the corresponding cyclopropane acids were determined. Changes in volume and energy associated with crystalline transformations and

with melting were measured. Data useful in analyzing for cyclopropenes and their derivatives were developed. A titration procedure was devised for determining cyclopropenes in small samples of oil. A nutritional study at WU involving rats fed cottonseed salad oil and partially hydrogenated cottonseed oils, all of which were Halphen-negative, was completed. No adverse effects were attributable to the cyclopropenes, even though the oils were fed at levels as high as 20% of the diet.

Contract research on the biological effects of cyclopropenoids is continuing at Ralston Purina Company, St. Louis, Missouri. The ingestion by laying hens of specially processed Halphen-negative cottonseed oils did not cause significant pathological lesions or have any significant effect on the composition of lipids of the heart, liver, plasma, or adipose tissues. The eggs produced by all the hens appeared to be normal, except for a possible depression in fertility. However, the ingestion of a refined cottonseed oil that was strongly Halphen-positive or a soybean oil supplemented with Sterculia foetida oil produced abnormalities in the eggs and resulted in increased ratios of saturated to unsaturated fatty acids in the lipids of the heart, liver, and adipose tissue of abdomen and gizzard. Surprisingly, these results were more pronounced in hens receiving 5% of the dietary oil than in those receiving 20%. Similar studies with reproducing rats, however, revealed that none of the above oils had a detrimental effect on reproduction or a significant effect on the fatty acid composition of the lipids of the heart, liver, plasma, or adipose tissues. These findings indicate that the special processes developed at SU for the inactivation of cyclopropenoids in cottonseed oil would be of industrial interest if the need should arise.

2. Detection, Estimation, Prevention, and Elimination of Aflatoxins. The method developed at the Southern Division for estimating aflatoxins in cottonseed products is now an official final action method of the Association of Official Analytical Chemists (AOAC). Stability studies on aflatoxin standards showed benzene:acetonitrile (98:2) to be superior to either benzene or chloroform for maintaining the integrity of primary standard aflatoxin solutions. Official AOAC aflatoxin methods have been revised to incorporate this solvent for standards and sample extracts. Cooperative research among SU, NU, FDA, and MIT has established reference standard molar absorptivity for determining the purity of a given aflatoxin preparation. Some 480 aflatoxin standards were distributed to both domestic and foreign research laboratories.

Severe interferences were encountered when present analytical methods designed for estimating aflatoxins in either cottonseed or peanut products were applied to mixed poultry, rabbit, and fish feeds containing cottonseed meals. Work has begun on a new and improved analytical system utilizing dilute acid:methylene chloride for the primary extraction phase, and a dual silica gel:alumina chromatographic column cleanup of the crude extract before estimation of aflatoxins by thin-layer chromatography. The results are promising: aflatoxins can be detected with confidence at levels as low

as 3-4 $\mu\text{g}/\text{kg}$ in most feeds. When applied directly to oilseed meals, such as cottonseed meal, the technique is faster than the present official AOAC method for aflatoxins in cottonseed products and yields much cleaner purified extracts for thin-layer chromatography.

In a P.L. 480 project conducted at Nagoya University, Anjo, Aichi, Japan, scientists are investigating the biochemical mode of action of aflatoxins and their biodegradation by plant cell systems. Aflatoxin B₁ was added to sweetpotato root slices as a 1.5×10^{-4} molar solution in 0.2% dimethyl-sulfoxide. The formation of the enzymes peroxidase, succinic dehydrogenase, and cytochrome oxidase in the injured plant tissue was not inhibited, but increase in the number of mitochondria was definitely inhibited. This result indicates that DNA replication was inhibited but the synthesis of the enzymes was not. After slices treated with aflatoxin B₁ were incubated for 24 hours at 28-33°C, quantitative thin-layer chromatography revealed that 30% of the aflatoxin had decomposed during incubation. A major component, designated "Compound G," appeared on the chromatographic plates. It fluoresced green under ultraviolet light, and probably was produced from the aflatoxin.

Laboratory-scale experiments have verified earlier reports on apparent destruction of aflatoxins in contaminated cottonseed meals by treatment with formaldehyde. After several meals containing 200 to 500 ppb total aflatoxins were treated with 1.5 to 2.0% formaldehyde for 120 minutes at 100°C, 20% moisture in the meal, the products contained 14 ppb aflatoxins or less. In the presence of formaldehyde, the moisture content of the cottonseed meal could be elevated to about 30% without formation of intractable gummy masses during heating and agitation in the reactor. Extraction of cottonseed meal with 80% isopropanol reduced the aflatoxin level from 1170 ppb to 18 ppb. Similar extraction with 90% aqueous acetone reduced the aflatoxin content of contaminated cottonseed meal from 1170 ppb to 7 ppb. An improved steam stripping procedure was developed to reduce residual solvent levels in the extracted meal to 20 ppm for isopropanol and to 2 ppm for acetone. These levels are well below those allowed by the FDA for isopropanol residue in fish protein concentrate and acetone residue in spice oleoresins.

Aflatoxins (428 ppb) in a contaminated cottonseed meal were evidently destroyed by formaldehyde treatments in a laboratory-scale reactor. At 30% meal moisture, heating at 100°C for 60 to 120 minutes with 1.5 to 2.0% formaldehyde, with or without 1.0% NaOH, yielded products in which no aflatoxin was detectable. However, this meal may have been more susceptible to destruction of aflatoxin than were other cottonseed meals previously treated.

Two meals treated with ammonia, one treated with methylamine, and one treated with methylamine plus sodium hydroxide were prepared from a contaminated cottonseed meal containing 334 ppb aflatoxins. Aflatoxins in each treated meal were 7 ppb or less. Rat feeding tests (28 days; 14% diet protein) indicated that protein efficiency ratio (PER) ranged from 1.07 to

1.42 grams gain per gram protein for the treated meals compared with a PER of 1.37 for high quality untreated meal. Rats fed the treated meals for 90 days (25% in diet) exhibited essentially normal growth, blood chemistry, and urinalysis. Biochemical evaluations and organ weights were about normal with exception of increase in liver weight for rats fed the meals treated with methylamine. The lowering of PER is not considered drastic, and the 90-day feeding revealed no acute toxicity. Two-year rat feeding tests as well as trout feeding tests will be required for meals processed with basic nitrogen compounds. Good correlations were obtained between the PER of the treated meals and the growth response of the microorganism Tetrahymena pyriformis W, indicating the practicality of this microbiological method for estimating the nutritive value of oilseed meal proteins.

Large-scale ammoniation of cottonseed meal contaminated with aflatoxin was conducted at a commercial cottonseed processing plant. There were 13 ammoniation runs, 9 with meal containing an average of 519 ppb aflatoxins and 4 with uncontaminated meal. In each run, 2000 to 2500 pounds of meal, moistened to about 12.5%, was treated with anhydrous ammonia under 43 to 50 psig pressure. Treatment time ranged from 25 to 38 minutes, and meal temperature from 220 to 270°F. Nine-hundred pound samples of contaminated and uncontaminated meals, both treated and untreated, were sent to WU for two-year animal feeding studies to conform with FDA protocol for evaluating aflatoxin inactivation procedures. The treated contaminated meals selected for feeding tests contained 4 ppb aflatoxins or less. Larger amounts of these test meals have been placed in cold storage until they are needed at WU.

3. Elimination of Salmonella. Cottonseed meals from various sources were examined microbiologically. Two serotypes of Salmonella, S. lexington and S. simsbury of group E, were in an experimental glandless cottonseed meal prepared commercially. Small-scale experiments showed that times and temperatures suitable for killing salmonellae present in flour prepared from the experimental meal and originally containing 9% moisture are: less than 14 days at 135°F, 14 days at 125°F, and 21 days at 115°F. Chemical analyses showed that nitrogen solubility was not significantly affected by any of these heat treatments. Nitrogen solubility averaged 96%. A large-scale experiment involving 30 bags of meal and 2 bags of flour, totaling 1,500 pounds, showed that salmonellae could be eliminated when held for 10 days at 132°F. These data are significant additions to the literature concerning heat sensitivities of various Salmonella serotypes under different conditions.

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PEANUTS

Problems and Objectives

The domestic peanut crop is used primarily in foods such as peanut butter, confections, bakery items, and roasted nuts. However, in recent years, much of the crop has been dried and cured artificially, partly to afford protection from contamination with mycotoxins but with the result that peanuts and their products do not always have the same desirable flavor as peanuts cured slowly in the field. Information is therefore needed on the relation of chemical constituents of peanuts to the flavor, aroma, and other properties of the processed products. In addition, new and improved products must be developed to extend domestic and foreign markets. Basic and applied research on peanut proteins is a particularly important requisite to this expansion. To assure that peanuts will continue to be utilized in food and feed products, they must be protected from contamination by fungi and mycotoxins.

Major objectives of the research are:

1. To identify chemical sources of the characteristic roasted peanut flavor and aroma.
2. To develop new and improved products and processes.
3. To expand domestic and foreign markets by tailoring products to meet preferences of the consumer.
4. To insure the safety and wholesomeness of peanuts and peanut products.

Progress

NEW AND IMPROVED FOOD PRODUCTS

A. Chemical Composition and Physical Properties

1. Reactions of the Proteins. At the University of Granada in Spain, P.L. 480 research is being conducted to determine the reaction rate of protein with carbohydrates in peanuts. Frying peanuts for 30 min. at 150°C caused more protein damage than roasting at the same temperature for the same time. Autoclaving peanuts at 2.5 atm. damaged the protein more than roasting under similar conditions. Heating peanuts caused decrease or disappearance of sugars and decreased total and available lysine. Arginine was the only other amino acid that decreased significantly on heating. A trained taste panel rated peanuts roasted under dry conditions higher in palatability than those roasted under moist conditions. The biological value

of raw American (Starr) peanuts was found to be 67.0. A new, ninhydrin-positive component appeared in the aminogram of peanut protein that had been heated with glucose.

B. Flavor

1. Factors Affecting Flavor and Aroma of Processed Products. Gas chromatographic conditions for analysis of roasted peanut aroma and flavor concentrates were improved to the extent that over 60 components were clearly evident. The flavor concentrates were prepared under mild conditions. Interference from water was minimized by freezing in the presence of an organic solvent. Loss or alteration of some components of the concentrates was observed during gas chromatography. Evidence was obtained to suggest that a number of components may be altered during staling of peanut butter. Some gas chromatographic peaks, not necessarily representing single components, increased during staling, whereas others decreased in relative magnitude. Some of these components were highly volatile; others boiled at relatively high temperatures.

Chromatographic evidence was obtained for about 30 carbonyl compounds in oil pressed from roasted peanuts. Several of these compounds are believed to be major contributors to peanut flavors. Derivatives of aldehydes and ketones were prepared in situ in the oil and then separated from the oil and from each other by thin-layer and column chromatography. Only about 12 carbonyl compounds have been reported previously. Some unreported compounds appear to be long-chain unsaturated fatty aldehydes. Spin blanching followed by electric eye sorting offers a unique opportunity to segregate peanuts contaminated with aflatoxin. However, the flavor of spin-blanced peanuts is reported to be unstable. Significant differences were observed in the ratios of comparable gas chromatographic peaks obtained by sampling head space gas over peanut butters prepared from spin-blanced peanuts and from the same lot of peanuts conventionally blanched. Peanut butters prepared from spin-blanced peanuts had a mild off-flavor, described as "tallowy." Quantitative differences also appeared in less volatile components of flavor concentrates. Preparation of flavor concentrates was scaled down to permit examination of much smaller samples of peanut butter.

C. Technology--Process and Product Development

1. Improved Low-Fat Peanut Products. The color and texture of partially defatted peanut products were improved by use of dextrose and enzymes. A new test devised for evaluating the texture of the peanuts was useful in improving partially defatted peanut products. Storage tests of raw pressed peanuts and raw full-fat peanuts were conducted at temperatures of 100°F; 100°F for 3 days, then storage at 35°F; 75°F; and 35°F. At planned time intervals, oil-roasted peanuts were produced from these raw materials and stored at 75°F. At 100°F, the raw pressed peanuts stored satisfactorily for 6 months and the full-fat peanuts for 5 months. At the other

temperatures, both types of peanuts stored satisfactorily for over 12 months. Tests are continuing. To minimize oxidation, a new process is being developed for the production of partially defatted peanuts whose interstices are filled with an inert gas instead of air.

EXPANSION OF FOREIGN MARKETS

A. Chemical Composition and Physical Properties

1. Properties of the Proteins. Effect of heat on major proteins and selected enzymes of peanuts was studied by disc and immunolectrophoresis. Mobility and antigenicity of all proteins except arachin changed drastically from 110 to 155°C. Protein solubility decreased. Some enzymes were heat-stable: allantoinase to 80°C, glutamate dehydrogenase and leucine aminopeptidase to 130°C. The protein efficiency ratio of the heated proteins in rat feeding tests was 1.9 for peanuts dry-heated at 120°C and 1.8 for peanuts wet-heated at 110°C (casein standard, 2.5). A nonspecific lectin from peanuts was purified by Sephadex gel chromatography. An apparatus was developed to concentrate solutions of proteins by reversible filtration using Sephadex gels. Proteins of the peanut cotyledon and embryo were compared by chromatography, electrophoresis, ultracentrifuge, and immunochemical methods. Results showed that α_1 -conarachin is cytoplasmic and α_2 -conarachin is particle-bound. α -Arachin and α_2 -conarachin predominate in the cotyledon within protein bodies.
2. Properties of the Lipids. Glyoxylate, a degradation product of fat and carbohydrate metabolism, was metabolized further by glyoxylate cycle enzymes located in the glyoxysomes (peroxisomes), subcellular particles in oilseeds. Allantoinase, a ureide-metabolizing enzyme that produces glyoxylate and urea in seeds, has also been found in glyoxysomes. Spherosomes, organelles found in cells of seeds and plants, were isolated intact from peanuts, cabbage leaves, and onions. Comparison by light and electron microscopy showed that the particles from each tissue had the same general size distribution and structure and that all contained lipids, confirmation that the spherosome is the site of storage of oils in seeds. Cottonseed miscella were treated with solutions of ferric chloride in acetone. Filtering the supernatant oil through clay to remove the iron-pigment materials yielded a colorless oil.

PROTECTION FROM POTENTIALLY HARMFUL MICROORGANISMS AND TOXINS

A. Microbiology and Toxicology

1. Detection, Estimation, Prevention, and Elimination of Aflatoxins. Serial transfer of single spore isolates of Aspergillus flavus was superior to customary mass spore transfer for maintaining relatively constant aflatoxin production by reference standard mold strains. An orange pigment produced in high levels by a mutant strain of A. parasiticus has been identified as norsolorinic acid (2-hexanoyl-1,3,6,8-tetrahydroxyanthraquinone).

Acidulation and heating of soapstocks containing aflatoxins B₁ and G₁ led to their conversion to relatively nontoxic hydroxy derivatives B_{2a} and G_{2a}. Model kinetic studies showed the conversion to be first order and extremely pH dependent. For maximum inactivation, soapstocks should be acidulated at pH 1 and heated at 100°C for about 10 minutes.

Studies on the inheritance of aflatoxin production in Aspergillus parasiticus, which lacks a sexual stage, were conducted via the parasexual cycle: mixtures of two mutant stocks with different spore colors and nutritional requirements were grown on minimal media, which did not support the growth of either mutant alone. The induced fusing of mycelia produced heterokaryons in which the nuclei shared common cytoplasm. When spores from heterokaryons were replated on minimal media, green spored and stable diploid colonies with no nutritional deficiencies were produced with low frequency from fusing of two haploid nuclei. However, when diploids were synthesized between aflatoxin producing and nonproducing strains of A. parasiticus, the diploids produced aflatoxins, indicating that aflatoxin production is a dominant character. Further studies on pigments produced by a yellow mutant of A. parasiticus indicated that at least three anthraquinone pigments are elaborated. Isolation of these pigments is in progress.

When Aspergillus flavus, A. parasiticus, Fusarium oxysporum, and Penicillium sp. were cultured on liquid media and the isolated dried mycelia subjected to gas-liquid chromatographic (GLC) pyrolysis, markedly different and characteristic decomposition patterns were obtained. However, GLC analysis of head space volatiles from the wet mycelia showed only two major volatile peaks from all four species; one peak was tentatively identified as due to ethanol. Culturing A. parasiticus on wetted shelled peanuts and conducting GLC on head space volatiles from the wet peanuts (27% moisture) yielded two major volatile peaks. The reduction of both peaks by 85-90% when the peanuts were air dried to normal moisture (6%) indicated that volatile mold metabolites were rapidly lost when wetted mold-damaged peanuts were dried and mold growth was suppressed.

To obtain a minimally heated, contaminated peanut meal for use in determining whether aflatoxins can be eliminated by the procedure for making isolates, kernels containing 119 ppb total aflatoxins were water blanched, dried under mild conditions, reduced to flakes, and defatted at room temperature with hexane. The fat-free flakes, which contained 70 ppb total aflatoxins, were used in preparing protein isolates. Although aflatoxin content of the isolates was reduced, it was not eliminated.

Although research on inactivating aflatoxins with basic nitrogen compounds has recently been confined to cottonseed meals, based on previous experience the treatments should also be applicable to peanut meals.

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CITRUS AND SUBTROPICAL FRUIT

Problems and Objectives

Advances in the citrus and subtropical fruit industry are needed to utilize the already large but increasing production of these fruits to the economic advantage of growers, processors, and consumers. Research should be conducted not only to relate chemical components of citrus to its natural flavor and color but also to solve problems caused by bitterness and other off-flavors in oranges and grapefruit. New products should be developed to use more fruit, to attract consumers, and to reduce shipping costs. A particularly important problem is to reduce water and air pollution from citrus wastes. Processing procedures and equipment must also be improved. In addition, rapid, sensitive, and economical tests of quality must be devised to assure that the most desirable qualities of citrus and subtropical fruit are conveyed to the consumer.

Important goals of the research are:

1. To develop new and improved products from citrus.
2. To identify the sources of undesirable flavors in citrus and to develop methods to prevent them.
3. To improve processing methods to preserve or enhance the natural flavor, color, and other desirable properties of citrus products.
4. To expand markets by tailoring products to meet the needs and preferences of consumers.
5. To reduce water and air pollution from citrus wastes.

Progress

NEW AND IMPROVED FRUIT PRODUCTS

A. Chemical Composition and Physical Properties

1. Relation of Ribonucleotides to Consumer Acceptability of Processed Products. In grant research conducted at the University of Florida, Gainesville, Florida, ribonucleotides in citrus are being evaluated for their potential in affecting the appeal of processed products to the consumer, controlling changes in the fruit, and providing an index of quality. Methods were developed for analyzing monomeric, slightly polymerized, and highly polymerized ribonucleotides. Studies on relative amounts in different citrus varieties with maturity and in citrus products indicated shifts from polymerized to monomeric forms with increased heat treatment. Shifts in type and amount of ribonucleotides were observed with changes in fruit

maturity and after degreening. Ribonucleotide content was also related to stability of orange juice cloud. Taste tests will determine the effect of ribonucleotides on product quality.

2. Estimation of Peel Solids. Development of an organic acid index to assess the amount of peel solids in citrus products is the goal of contract research conducted at the Stanford Research Institute, Irvine, California. Data are available for the percentages of segment juice, rag, peel juice, and pressed peel from 13 lots of oranges (7 varieties, 4 geographical origins) and 10 lots of grapefruit (4 varieties, 4 geographical origins). Values for amounts of total free acids, total combined acids, and amounts of free and combined oxalic, malonic, succinic, malic, and citric acids were determined for each of the four components of each lot of fruit. No oxalic acid (free or combined) was found in segment juice from oranges or grapefruit; combined oxalic acid was always found in pressed peel from oranges and usually in pressed peel from grapefruit. Seasonal variations in acid content and distribution were at least as great as varietal. Storage of fruit for periods as long as 30 days, high extraction pressure, canning, or freeze concentrating had no effect on the oxalic acid content of the juice. Results indicated that oxalic acid can serve as a qualitative index to indicate the presence of peel in oranges. No other acid showed promise as a peel index.

B. Flavor

1. Improved Flavor and Quality. In a study of the relationship of ethylene formation to leaf abscission in freeze-damaged citrus, seedlings frozen for 4 hours produced small amounts of ethylene but no leaf abscission at 20°F; larger amounts of ethylene and 20% leaf abscission at 21°F; and still larger amounts of ethylene and 87% leaf abscission at 22°F. Plants treated at 20°F with 10 ppm ethylene for 24 hours had no leaf abscission; at 21°F and 10 ppm for 24 hours, there was 6% leaf abscission. The formation of ethylene was dependent on presence of oxygen. Fruit set in early February and late March 1969 differed greatly in size and in content of bitter flavanones during subsequent growth. Fruit set latest sized least and accumulated smaller amounts of bitter flavanones than fruit set earlier but having equal age or harvest date. Time of fruit set is one of several factors that determine the flavanone content of grapefruit during different crop years. Flavanones and/or precursors supplied to developing grapefruit decline as leaves mature. The factors cited affect the yield of citrus fruits and the chemical and sensory characteristics of their processed products.

Enzyme reactions are being evaluated for their potential in enhancing the flavor of citrus products. Commercially mature oranges and grapefruit were shown to contain enzymes that convert malic acid to ethanol. The increased activity of these and functionally related enzymes when citrus fruits were heated in an oxygen-depleted environment lowered juice acidity. These findings could lead to development of a process for treating citrus fruit

with natural compounds to make juices sweeter. Degradation of cloud by native pectinesterase in orange juice was shown to depend on juice-soluble pectin. This pectin can be removed from the juice by biochemical methods without heating. These findings could lead to development of a cold-processed juice having natural citrus flavor characteristics. An enzyme in orange juice was shown to catalyze the equilibrium reaction between primary alcohols and their aldehydes. Since these alcohols and aldehydes are constituents of orange essence, this enzyme may be important in the natural development of the characteristic flavor of orange juice.

Samples of distilled orange essence oil prepared commercially from juice were similar in composition to those prepared from orange peel products. In aqueous grapefruit essence, thirty-two volatile flavor compounds were identified, twenty-three of which were found for the first time as constituents of grapefruit juice. Seventeen compounds were identified from the carbonyl fraction of cold-pressed grapefruit oil. This fraction differed significantly from the corresponding fraction in orange oil, having a larger number of esters. A new citrus constituent, nootkatene, was isolated from cold-pressed orange oil. An improved method for analyzing aqueous essence was developed. About 25 μ l of the aqueous essence was injected directly onto a gas chromatographic precolumn containing porous polymer beads. Thus the water was separated from the more tightly held flavor components, which were then collected in a cold trap and injected directly from the trap onto a second column for further separation and analysis. Since solvent extraction is not required, this method is especially useful for quantitative analysis.

Frozen concentrated orange juice made with different yields was prepared for organoleptic and chemical analyses to determine the relation of yield to compounds affecting flavor. Samples of peel oil desludger effluent containing high quantities of peel components were concentrated and frozen as sources of these components. Gas and thin-layer chromatographic procedures were developed for separating and identifying the components of interest.

Research being conducted in cooperation with the Florida Citrus Commission and the Western Utilization Research and Development Division is directed toward developing flavor concentrates to improve foam-mat dried and other citrus products. Steam stripping, fractional extraction, distillation, and steam distillation procedures were applied to late season fruit and to citrus wastes, including rag, peel, ground fruit, and peel oil desludger effluent. Fractional distillation procedures were developed for concentrating the aromatic and flavor components. Dehydrated and concentrated juice products containing these flavor concentrates were prepared. Comparison with controls indicated considerable improvement in quality. Chromatographic methods were developed for comparing flavor and aroma fractions of essences and oils obtained under different conditions to assist in determining optimum operating conditions. The distilled oil recovered from peel oil desludger

waste is of high quality because it is rich in volatile aromatics and thus appears to be in high demand. The quality of the aqueous aroma solution is also high.

2. Prevention of Deterioration of Flavor. Research is being conducted on the elaboration of lipid constituents in citrus juice and their contribution to the development of off-flavor and off-odor in commercially processed juice. Chilled orange juice stored for 16 months had a threefold increase in free fatty acids at 40°F and an eightfold increase at 85°F. Examination of the neutral lipid and polar lipid fractions showed that approximately 95% of these free acids were derived through enzymic hydrolysis of phospholipids. Decreases in the four major phospholipids--phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl serine, and phosphatidyl inositol--ranged from 46 to 91% in juice stored at 85°F. The production of large quantities of free unsaturated fatty acids at elevated storage temperatures predisposed commercial orange juice to development of off-odor and off-flavor. Thus, although unsaturated fatty acids, which comprise approximately 80% of the total fatty acids in orange juice, contribute very little to off-flavor, their importance is that they function as precursors for many volatile off-flavor compounds. Study of other components is also in progress: nitrogen stripping of volatiles, chemical trapping of carbonyls as dinitrophenylhydrazones (DNP), GLC analysis of these carbonyls, and mass spectral verification of GLC peaks. By use of an efficient carbonyl regeneration procedure for DNP derivatives, the GLC analysis remained as direct as though the free carbonyls themselves had been trapped. Although none of these techniques are new, it is possible that this particular combination is being used for the first time.

In contract research at Ohio State University Research Foundation, Columbus, Ohio, a gas chromatographic method was developed for analyzing volatile derivatives of sugars, amino acids, and sugar-amine complexes. This method indicated formation of three specific intermediates during nonenzymic browning. These intermediates increased under specific conditions. Approaches developed for blocking their formation included removing two specific amino acids, γ -aminobutyric acid and arginine; controlling water content to well below 5%; maintaining pH at about 5 to 6; decreasing content of potassium ions; and decreasing or removing the simple sugars d-glucose and d-fructose. These treatments were suggested as ways to improve storage stability of dehydrated citrus juice products as well as most liquid food products that contain high levels of sugar and acid.

C. Color, Texture, and Other Quality Factors

1. Extracts from Peel to Enhance Color. The extraction and concentration process reported previously--obtaining highly colored concentrated extract from orange peel, treating it to remove factors that interfere with color or flavor, and adding it to orange juice products--was applied to most commercial varieties of oranges, tangerines, and tangelos. Highest color

yields were obtained from the commercial orange varieties Pineapple and Valencia. Color concentrates were stable more than six months when stored at -5°F in the dark. Orange juice products with color added had stable color for as long as six months when stored at the conditions usually recommended for the respective products.

D. Technology--Process and Product Development

1. Control of Bitter Constituents in Citrus. Naringin content of commercially processed grapefruit juice was determined on all available early season packs, at weekly intervals from five selected plants for the entire season, and at regular intervals during a day-long continuous run at three plants. Also, fruit of three important grapefruit varieties was harvested at monthly intervals from each of three geographical areas, and naringin determined from the flavedo, juice, rag, and albedo of each sample. Naringin content in all parts of the fruit tended to decrease with maturity; in commercial juices, it was affected by plant practices. Variations in a given plant on a single day late in the season were mostly randomized between 350 and 550 ppm naringin. Limonin content of the juice from 13 varieties of lemon, 6 varieties of orange, and 16 varieties of tangerine and its hybrids was less than 3 ppm, well below the taste threshold. The Murcott was the only orange having sufficient limonin (as much as 19 ppm) to limit its suitability for processing. Grapefruit juices decreased in limonin content from as high as 15 ppm in November to 3 ppm in April. Effects of variety and location were greater than the effect of rootstock.

2. New and Improved Products from Citrus and Subtropical Fruit. The process for preparing puree from comminuted whole citrus fruit has been improved. Steps are: (1) ten-minute water blanch at 212°F; (2) coarse grinding with a revolving knife-type mill through 0.5" screen; (3) paddle finishing through 0.060" screen to remove seed and tough peel and rag; (4) homogenizing; (5) heat treating to prevent clumping; and (6) hotpacking and cooling. Recoverable oil of purees ranged from 0.12 to 0.69%, enough to impart distinct citrus flavor to beverages containing from 5 to 10% of the whole fruit purees. Clouding characteristics of orange purees were demonstrated. Ten percent orange puree in solution gave transmission readings of 16 to 20%, which approximates readings from single strength juice. Both grapefruit and orange drinks prepared from whole fruit purees were acceptable after one year's storage at 65° to 95°F. Seasonal variation and varietal studies indicated that juice quality can be used to predict the quality of the puree.

Further studies on retention of volatile materials during freeze drying indicated that 50-60% could be retained if samples were finely divided and freeze drying rate was fairly high. In coarsely divided products, which require longer drying times, retention of volatiles was not as great. This result indicated that freeze dried materials might be used for flavor enhancement if they are prepared properly.

ABATEMENT OF POLLUTION

A. Technology--Process and Product Development

1. Recovery of Peel Oil and Essence from Waste. The objective of contract research at the University of Florida, Gainesville, Florida, is to develop a system that will permit maximum recovery of oil and essence from citrus peel oil desludger waste with a minimum percentage of vaporization and a minimum of time at elevated temperature. The oil recovered by this system is very fragrant and far superior to the previously available distilled oil. Also, the aqueous essence is currently in great demand. Removal of these materials will decrease the organic matter by 25 to 35%, reduce objectionable odors, and retard bacterial growth.
2. Reduction of Air Pollution from Citrus Feed Mills. In contract research by Fiske-Gay Associates, Inc., of Orlando, Florida, tests on extent of air pollution, energy efficiency, and materials balance of peel driers are being conducted at three plants of different design, three tests being scheduled at each plant. Two plants with a waste heat evaporator and with driers that provide for recirculation of air are well below the tolerance for air pollution. The third plant, which has an air scrubber only on exhaust gases, has improved but is still over the tolerance. This plant is being remodeled and is expected to be within acceptable limits next time. The throughput on the two recirculation driers will be increased, and emission and efficiency again checked. This study will demonstrate different ways of adequately controlling air pollution and the cost of each method. The scrubbing system will interest small concerns that cannot afford a waste heat evaporator.

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VEGETABLES

Problems and Objectives

The market for fresh vegetables has suffered from the effects of rapid spoilage, seasonal surpluses, and increasing demand for convenience foods. Stable, attractive, and convenient processed vegetable products must therefore be developed. However, much research is needed to solve problems incurred in the processing. For example, although most of the cucumber crop is brine-cured, spoilage during curing frequently causes high losses. To increase the utilization of dehydrated sweetpotatoes, their shelf-life should be extended and new products developed to combine the flakes with other foods. Celery, already an important flavoring ingredient, could become much more widely used if factors responsible for variations in the intensity of flavor could be controlled during processing and if more convenient products were developed. To improve processed vegetables, there is also need to determine the effect of climate, soil, cultural practices, and variety upon the raw material, particularly for vegetables like tomatoes, in which color, flavor, and texture are frequently poorer when they are grown in warm instead of temperate regions. In addition, processing methods should be modified to reduce pollution.

More specific objectives of the research are:

1. To identify the effect of different characteristics of raw vegetables on quality of the processed products.
2. To improve processes for fermented vegetables, particularly cucumbers.
3. To modify and enrich products from sweetpotato puree and flakes.
4. To develop products having improved natural celery flavor.
5. To develop new and improved products from other southern-grown vegetables, such as tomatoes and carrots.
6. To reduce pollution from processing wastes.

Progress

NEW AND IMPROVED VEGETABLE PRODUCTS

A. Flavor

1. Prevention of Deterioration of Quality. When dehydrated vegetables containing relatively large amounts of β -carotene were exposed to oxygen, they simultaneously lost carotene and developed off-flavor. Carotene alone was not responsible for the off-flavor, but its interaction with other lipid material was a factor. β -Carotene in dehydrated sweetpotato flakes (DSF) was

present in at least two fractions, water dispersible (WD) and nonwater dispersible. The WD fraction contained 15-20% of total carotene, polar and neutral lipids, and starch. The ratio of lipids to carotene was 60:1. Spectrophotometry indicated that the carotene was dissolved in the other lipids. Autoxidation of carotene in DSF can occur as a coupled reaction with the lipid fatty acids. Studies of DSF stored in air indicated that the WD carotene fraction was oxidized more rapidly than was the non-WD fraction. These studies also showed that 60 to 70% of the carotene in DSF was not destroyed after storage for a year. Evidently, substances native to the sweetpotato protect this carotene from oxidative attack. This research is conducted in cooperation with the North Carolina Agricultural Experiment Station.

B. Technology--Process and Product Development

1. Fermented Cucumber and Other Vegetable Products. Research is continuing on controlled (pure culture) bulk fermentation of vegetables for reprocessing. The basic principles are the same as those used for in-container products. Main differences are: use of L. plantarum, a species that produces high levels of acids; chemical instead of heat sanitizing; incorporation of food organic acids and buffering compounds to favor and stimulate growth of the introduced culture; and maintenance of brine temperature close to the optimum of that required for the introduced culture. Four major experiments representing 98 lots (1-60 gal.) provided data on fermentation characteristics at controlled temperature. The successful completion of these studies and adaptation by industry will reduce processing losses and waste disposal problems. Salts such as potassium chloride, ammonium nitrate, potassium nitrate, magnesium sulfate, and ammonium sulfate, tested as substitutes for sodium chloride at concentrations of 3, 6, and 9%, show promise for brine curing. Resulting spent brines might be used as liquid fertilizer and thus become beneficial to the environment. Various phases of this research are conducted in cooperation with the Pickle Packers International, Inc., and the North Carolina and Michigan Agricultural Experiment Stations.

2. New and Improved Sweetpotato Products and Processes. A practical assay for the determination of alpha-amylase in sweetpotato processed juice was developed to guide the adjustment of processing variables and thus to control uniformity in sweetpotato flakes. This modified procedure, which requires only basic laboratory equipment, is applicable to roots peeled in lye as well as by hand. GLC aromagrams of baked and otherwise processed sweetpotato products are being compared with subjective determinations. Application of high-temperature, short-time sterilization procedures helped to minimize the undesirable tart taste of canned sweetpotato puree. Since ingredients in sweetpotato pie mix have been changed to overcome variations in properties of commercial flakes, production by industry may now be practical. An important facet of this research is now directed toward abating pollution. The dry caustic peeling process developed at the Western Division has been applied to sweetpotatoes, and successful trial runs have been conducted at

a sweetpotato plant. Commercial application of this development is dependent upon economic considerations.

3. More Flavorful Dehydrated Celery Products. Research has continued on the previously reported process for recovering essential oil from fresh celery waste. The flavor and aroma of this oil closely resemble those of fresh celery. Yields were as high as 250 ml of essential oil per ton of waste. For the first time, studies of the chemical composition of the oil have provided positive identification of the most abundant flavoring constituents: 11 hydrocarbons, 13 alcohols, and 17 carbonyls were identified as constituents of fresh celery. Approximately 35 of these compounds have not been reported previously as constituents of fresh celery.

4. Improved Tomato and Other Vegetable Products. Alcohol-insoluble solids (AIS) were determined for Homestead, Chico, Chico Grande, LaBonita, and Chico III varieties of tomatoes. Higher values for total AIS were obtained for the firmer canning types, whereas higher protein values were obtained for the softer fresh-market types. To reduce enzyme degradation of the pectins, tomatoes were frozen in liquid nitrogen in preparing the marc for AIS. Methods for extracting pectic substances from AIS were evaluated. Amounts extracted varied with the sequence of extraction with water, .02% ammonium oxalate, and .05N hydrochloric acid. After a triple extraction with each of these three solvents in the order listed, an additional fraction could be extracted with .05N sodium hydroxide. Each fraction was resolved by the use of gel filtration techniques into two or more subfractions, which represent compounds of different molecular size. Studies are continuing on the molecular nature of the pectic substances in soft and firm varieties of tomatoes to provide information for improving processing and products.

Peel ruptured and could be easily removed from Chico, Chico Grande, LaBonita, and Homestead-24 varieties of tomatoes that had been submerged from 20 to 40 seconds in a 42% calcium chloride (CaCl_2) solution at 250°F. Time of submergence until rupture and amount of CaCl_2 absorbed were not consistent among the varieties. To be made commercially feasible, this process will require developmental studies. At the end of 5 days' storage at 40°F (refrigerator), fresh tomatoes that had been peeled in liquid nitrogen and sealed in polyethylene bags were as good as freshly hand peeled tomatoes and were considerably superior in firmness and flavor to tomatoes peeled in hot water and stored under similar conditions. Canned seasoned salad pack tomato products (Chico and M-121) that had been peeled in liquid nitrogen were firmer and crisper than tomatoes peeled in hot water. Different acids are being evaluated for lowering the pH of salad packs to 3.6 to avoid harshness.

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NAVAL STORES

Problems and Objectives

Naval stores are unusual agricultural products in that they are used almost exclusively as chemical raw materials. Although rosin, turpentine, and pine gum consist of organic compounds with unique chemical structures that are difficult to duplicate synthetically, these naval stores products face increasing competition for markets from products derived from petroleum and coal tar. Research is needed to retain or expand industrial markets for naval stores, particularly in large-volume outlets such as polymers, plastics, elastomers, resins, plasticizers, surface coatings, adhesives, textile finishes, odorants, and agricultural chemicals. Although about one-third of the rosin produced in this country is already exported, research to convert rosin to more expensive derivatives would not only increase the value and the amount of rosin exported but also benefit domestic markets.

Major objectives of the research are to develop:

1. Basic knowledge of the composition and properties of pine gum, rosin, turpentine, and their derivatives.
2. New and improved chemical intermediates from rosin, resin acids, terpenes, and pine gum.
3. New and improved industrial products--particularly polymers such as polyurethanes, polyesters, and polyamides--from rosin, turpentine, and pine gum.

Progress

NEW AND IMPROVED FOREST PRODUCTS

A. Chemical Composition, Physical Properties, and Structure

1. Composition and Properties of Pine Gum, Rosin, Turpentine, and Derivatives. The neutral fraction of gum rosin was shown to contain more than 50 components. The major products were diterpene aldehydes and alcohols corresponding to the acids present. A gas chromatographic method for the analysis of oleoresins and rosin was developed. The composition of the acid portion of practically all of the commercially available rosins and pine oleoresins was determined. Since these analyses represent the best information now available on this subject, there has been a worldwide demand for the publication giving this information. Sandaracopimamic and Δ^8 -isopimamic acids were shown to make up about 3 to 4% of most commercial rosins. Improved methods were developed for the isolation and purification of several resin acids. A method for identifying and analyzing for the terpene alcohols of pine oil was developed. The methods of analysis developed were used to determine the composition of the material extracted from pitch-soaked

ponderosa pine stumps. Although some work has been done on ponderosa turpentine, very little information was available on the rosin, pine oil and sesquiterpene fractions extracted from these stumps.

B. Technology--Process and Product Development

1. Chemical Intermediates from Rosin, Resin Acids, Terpenes, and Pine Gum. Research is in progress to investigate the preparation of commercially useful derivatives from the oleoresin of ponderosa pine stump-wood. A plant-scale run on Arizona stump-wood was made in cooperation with a commercial processor in Florida. This run produced 128 drums of F.F. wood rosin and 2100 gallons of liquid products, and showed that these stumps could be processed on present equipment. Paper size was prepared from 44 drums of this rosin, and arrangements were made to have this paper size evaluated at a kraft paper mill. A commercial firm has agreed to fractionate 100 gallons of the pine oil produced. All four products--rosin, pine oil, dipentene, and turpentine--from ponderosa stump-wood differ from present commercial products. The rosin has a lower acidity and a higher neutrals content than the present F.F. rosin. The pine oil fraction contains 20-40% longifolene, and the turpentine contains carene. The value of longifolene is greater than that of pine oil and should more than pay for fractionating it from the pine oil. Although carene is not present in American turpentine, it is present in most European turpentine and should not interfere with some of the uses for this product. It should be possible to modify the rosin derivatives so that they will meet the present requirements.

Much information of scientific value has been obtained in research on the application of photochemical reactions to naval stores products. Acid and base had little effect on the photochemical addition of alcohols to methyl-abietate or 2,4(8)-*p*-menthadiene but were controlling factors in the addition of methanol to methyl neoabietate (MNA). In the presence of acid, addition of methanol to MNA was accompanied by an unprecedented loss of hydrogen. Photolysis of 2,4(8)-*p*-menthadiene in pentane yielded an unusually stable bicyclobutyl compound that can be used to prepare a variety of new terpene derivatives. Photolysis at 2537 Å of α -pyronene and the two alloocimenes obtained by pyrolysis of α -pinene showed that some conclusions of earlier workers regarding the primary reactions are incorrect. Although steric effects have received little attention as a factor in determining the products of a photochemical reaction, our findings with α -terpinene indicate that they can be the controlling factor. These results have significance in the application of photochemical processes to conjugated fatty acids, steroids, and other polyenes, as well as to terpenes and resin acids. Significant progress has been made in delineating the reactions involved in the oxidative color degradation of abietic acid and rosin.

In contract research at Battelle Memorial Institute, Columbus, Ohio, the acid-catalyzed process for the dimerization of rosin was studied in detail. Catalysts studied included sulfuric acid, aluminum chloride, zinc chloride, and boron trifluoride. The most important dimerization conditions were

determined to be the solvent employed, the acid strength of the catalyst, and the ratio of solvent-to-sulfuric acid-to-rosin used. Details of the process were worked out using pure abietic acid. Yields of dimer from abietic acid were as high as 90%. The yield is limited by a side reaction involving disproportionation of starting materials. A tentative mechanism for the dimerization was developed. Structures were postulated for some of the major resin acid dimers present. Purification of rosin dimer was achieved by low pressure distillation. The purified rosin acid dimers were converted to polyamides, which have been evaluated as modifiers for epoxy resins. It is anticipated that most of the current manufacturers of rosin dimer acids will find this process study of definite value to their commercial operations.

A new type of dibasic acid has been prepared from rosin by catalytic decarboxylation followed by reaction of the dienic hydrocarbon with fumaric acid or maleic anhydride. This product has been shown to be useful in the preparation of modified styrenated polyester resins for laminating. Initial screening tests indicated that phosphoric acid was a superior catalyst to use in the decarboxylation step. It was found that phosphorous pentafluoride (PF_5) smoothly decarboxylated dehydroabietic acid at room temperature and atmospheric pressure. Two major products were obtained. The effect of PF_5 on gum rosin and the other resin acids is under investigation. It has been observed that PF_5 is also an excellent esterification catalyst for resin acids. The resulting esters are stable to decarboxylation. A series of rosin-based polyesters that have been prepared show promise as rubber tackifiers, which are used in the manufacture of most automobile tires. Testing is being done by outside agencies.

Heating potassium or methyl levopimарате at 200°C in the presence of excess potassium hydroxide or of a molar amount of free radical initiator has been shown to open up the rings of the resin acid molecules. This is the first reported controlled ring opening(s) of the partially hydrogenated phenanthrene nucleus, found in the resin acids of rosin. Four new compounds were obtained, and their structures have been established. The mixture has been ozonized to yield a product useful as a fungicide. The reaction has been shown to be general in nature for specific types of substituted cyclohexadiene ring systems. The pyrolysis of benzene solutions of gum rosin, levopimamic acid, abietic acid, dehydroabietic acid, and methyl dehydroabietate was carried out at 800°C in a hot tube. The ester was also run neat. Eleven major compounds were isolated and identified. Four of the products were shown to be reaction products of the rosin and the benzene solvent. The results indicate that rupture of the resin acid molecule is occurring at the A ring, preceded by decarboxylation and dehydrogenation.

Methods were developed to prepare new amino alcohols, amino acids, diamines, and diisocyanates with industrial value from some potentially cheap resin acid derivatives. Diamines, glycols, and amino acids may have use as intermediates for condensation polymers. Currently, the selling price for high-grade diisocyanates ranges from \$.88 to \$3.50 per pound; rosin diisocyanates

could undoubtedly be made within this range. The rosin-derived diisocyanates were shown to react with glycols to give polyurethanes which, by visual examination, appeared to be quite satisfactory, tough rubbery materials. The research involved a study of the conversion of 12-hydroxymethylabietic acid to 12-aminomethyl- and 12-aminoethylabietanoic acids and modifications resulting from replacement of the acid function with amide, nitrile, amino-methyl and hydroxymethyl groups. In one instance, unexpectedly, hydroxyl elimination from the hydroxymethyl group resulted in loss of functionality.

2. Industrial Products from Rosin, Turpentine, and Pine Gum. Procedures devised for increasing the functionality of resin acids by addition of hydroxymethyl groups have led to valuable new hydroxy acids and glycols. Thermosetting and thermoplastic polyurethane films were prepared from poly-propylene glycol polyethers and hydroxyl-terminated polyesters of resin products. The stepwise addition of the resinyl moiety (the actual resin, not the polyether or polyester) at levels as high as 25% increased strength, modulus (stiffness), and brittleness. Tensile strengths from 4 to 8 thousand pounds were easily obtained. Rigid foams and films comparable to commercial ones were prepared by industry from the glycol ester of 12-hydroxymethylabietenoic acid and 12-hydroxymethylabietanol and proved acceptable. Effective liquid-liquid countercurrent extraction procedures were developed for separating hydroxymethylated resin acids from unreacted components in the following systems: oxonated rosin; the reaction of rosin with formaldehyde in acetic acid; and the reaction of pine gum with formaldehyde. The separations are practical, cheap, and should do much to interest industry in these materials.

Research has been conducted to produce stocks of 12-aminomethyl- and 12-aminoethyl-derivatives of abietanylamine for conversion to diisocyanates to be used in preparing polyurethanes in in-house research and condensation polymers (polyamides) in related contract research. The general method employed involved reacting 12-hydroxymethylabietenoic acid with thionyl chloride (Vilsmeier reaction) and converting the resulting 12-chloromethyl-abietanyl chloride to the diamine. Difficulties encountered in scaling up the process have been overcome. A new method for preparing diamines and consequently diisocyanates resulted from the reaction of the ditosylate of the ethylene glycol ester of 12-hydroxymethylabietanoic acid with ammonia. The diamine was easily converted without decomposition to the diisocyanate. Materials cost for such a compound is of the order of 25¢ per pound.

The polymerization of terpene monomers to obtain new condensation-type polymers is being investigated in contract research at the University of Arizona, Tucson, Arizona. Polyesters and polyurethanes of pure 12-hydroxymethylabietanoic acid and 12-hydroxymethylabietanol all had low molecular weights (inherent viscosities, approx. 0.2). End group determinations indicated the presence of reactive functional groups and, for some reason, the polymerizations stopped. X-ray studies are planned to ascertain the difficulties. Work along these lines will be directed toward modifying conventional polyesters, polycarbonates, and polyamides. Spandex-type fibers

(elastomers) are composed of alternate rigid zones and elastic zones within the polymer molecule. Similar results should result by coupling isocyanate-terminated polymers with 12-hydroxymethylabietanol in one step. A commercial dimerized rosin was easily converted to a diisocyanate by reacting the acid chloride with ethanalamine hydrochloride and then phosgene. Difficulty was experienced in preparing acrylo- and fumaropimamic acid chlorides for this reaction.

In a completed contract project at Battelle Memorial Institute, a number of new classes of naval stores derivatives were found to be useful in various areas of the adhesives field. In all four areas of adhesives tested, the activity of the new products was equal or superior to that of commercial products. One of the most promising was a new type of rosin-based polyester that was active in rubber tackifiers, pressure-sensitive adhesives, and ethylene-vinyl acetate hot-melt adhesives. These leads provide starting points for the development of a whole series of new types of naval stores products for the adhesives industry. After pilot-scale evaluation, a resin manufacturer has advertised two of the rubber tackifiers, and a potential user anticipates a starting market of over three million pounds annually.

Vinsol (a crude mixture containing resin acids), ligninsulfonate (a byproduct of the sulfite-paper industry), and tall oil pitch (the residue left after distillation of crude tall oil) have been used as admixtures to improve the properties of concrete. Because published information indicated that rosin derivatives might also be effective admixtures, contract research was initiated at Battelle Memorial Institute to prepare some 20 derivatives of rosin and to select those materials having the greatest promise as additives for further evaluation. None of the materials were effective as water-reducing and set-retarding agents for concrete. However, the sodium salts of gum rosin and of acrylic-, maleic-, and fumaric-modified gum rosins were more effective air entraining agents than the sodium salt of Vinsol, a commercial air entraining material. The acrylic-modified material was most efficient and possibly will compete economically with Vinsol. An evaluation of the acrylic-modified rosin by industry is planned. A commercial sample of fumaric-modified tall oil rosin behaved very poorly.

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SUGARCANE

Problems and Objectives

A paradoxical situation exists in the refining of cane sugar: an increasing amount of colorants and other impurities in raw sugar but an increasing demand for exceptionally white and high-quality refined sugar. The result, of course, is that the technical difficulty and cost of refining have also greatly increased. Moreover, present refining procedures do not always remove impurities from even the better quality raws. Some batches of refined sugar have been rejected because they contained such impurities or because they caused floc in bottled beverages. However, the chemical nature of some of the impurities is not yet understood sufficiently to permit techniques for elimination to be devised. Nor is the chemistry of the refining processes themselves well defined. Research is therefore needed to increase the yield and purity of refined cane sugar.

Objectives of the research are:

1. To identify colorants in cane sugar and develop a practical method for removing them during refining.
2. To evaluate innovations in filtration, fractionation, and coagulation for removing impurities that leave a high ash content in refined sugar.
3. To develop unit processes that are less costly with respect to time, labor, and equipment.

Progress

NEW AND IMPROVED FOOD PRODUCTS

A. Chemical Composition and Physical Properties

1. Identification and Control of Colorants. Cooperative research with the Cane Sugar Refining Research Project, Inc., is just getting underway. A spectrophotofluorometer is being evaluated for measuring fluorescence of sugar products at different wavelengths. The technique, if adaptable, will be of value in confirming the identity of the fluorescing impurities and in maintaining quality control in sugar manufacture. Limited tests on cane juice, raw sugar, molasses, and first and fourth strike granulated (refined) sugar are encouraging in that easily measured differences were demonstrated.

Publications

None

SWEET SORGHUM

Problems and Objectives

The Lower Rio Grande Valley, which is largely dependent on an agricultural economy, must have a greater selection of crops for diversification to meet unfavorable environmental and marketing conditions that frequently beset the area. One of the crops that have potential for providing profitable diversification is sweet sorghum, particularly since new disease-resistant varieties with high sugar content are now available. The modest water requirements of sorghum and the subtropical climatic conditions conducive to an extended growing season also increase its attractiveness. In addition, integration of the processing of sorghum with that of beet and sugarcane would permit greater use of costly installations in sugar factories. However, to achieve these goals, research is needed to develop practical methods for the recovery of sugar from sweet sorghum.

More specific objectives of the research are:

1. To identify major constituents and compositional changes that affect sugar recovery in relation to variety, cultural practice, environment, time of harvest, and handling after harvest.
2. To explore chemical and physical procedures for removing nonsugars from sweet sorghum juices.
3. To develop an economical process to recover the sugar from sweet sorghum.
4. To evaluate the processing characteristics of newer sorghum breeding lines grown under different agricultural practices.

Progress

NEW AND IMPROVED FOOD PRODUCTS

A. Technology--Process and Product Development

1. Recovery of Sugar from Sweet Sorghum. Treatment with commercial α -amylase and a coagulation and settling procedure were compared in laboratory and pilot-plant studies for efficiency in eliminating the starch that escapes sweet sorghum juice clarification. By either procedure, the starch content was satisfactorily reduced to approximately 0.04% of the solid content of the product syrups, a level at which its interference with sugar recovery should be negligible. The sedimentation procedure not only was the more economical but also provided syrups with less organic matter, which would adversely affect sugar recoverability. In laboratory and field evaluations of new sweet sorghum breeding lines, two high sucrose varieties,

Mer 64-3 and Mer 65-2, indicated promise of extending the potential harvest season well into November in South Texas. These two varieties require about two weeks longer than the standard variety, Rio, to attain maximum maturity and tonnage.

Sweet sorghum processing units are being assembled into an integrated pilot-plant facility for study of the operations required to produce raw sugar from the extracted plant juices. This facility should be available for process testing during the 1970 sorghum harvest season in South Texas. On a semi-pilot-plant scale, procedures are being developed to increase the removal of aconitic acid from syrups before sugar crystallization. One factor affecting the yield of insoluble aconitates was an insufficiency of available magnesium ions in some of the juices. Addition of soluble magnesium salts improved the elimination of aconitates to approximately 50%, a level that should minimize their adverse effect on the recovery of raw sugar. Laboratory and field evaluations of the various sweet sorghum nursery and varietal materials planted in South Texas during 1969 provided data that encourage expansion of the varietal studies to six lines.

Various phases of this research have been conducted in cooperation with the Texas Agricultural Experiment Station, Crops Research, and the Louisiana State University Department of Chemical Engineering.

Publications

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RICE

Problems and Objectives

In the United States, the capacity for producing rice has increased faster than domestic consumption and exports. Detailed knowledge of chemical composition and physical properties of rices is needed to guide milling, processing, and product development. New and diverse food products that are economical to manufacture, convenient to prepare, and attractive in flavor and texture must be developed to increase the consumption of rice both domestically and abroad. Research is also needed to devise methods of treating rice to alter its cooking and processing characteristics for specific end uses.

Current objectives of this research are:

1. To identify the characteristics of the untreated or treated, whole or fractionated kernel that may be used to predict potential commercial uses.
2. To develop practical procedures for preventing or sealing checks and altering plasticity of rice kernels to improve milling yields.

Progress

NEW AND IMPROVED FOOD PRODUCTS

A. Technology--Process and Product Development

1. Increased Milling Yields. A relationship was found between the percentage of rough kernels showing fissures in x-ray photos and the percentage of broken kernels observed after milling. For long-grain rice, the number of brokens after shelling and hulling was 2 and 3 times greater, respectively, than the number of fissures revealed by x-rays. For medium-grain rice, however, the number of brokens after shelling was only one-half the number of fissures observed, and, after hulling, essentially the same as the number of fissures. Some of the kernels showing minute fissures were resistant to breakage. Breakage is influenced by grain type and can be predicted by this x-ray technique. Lowering the temperature of brown rice to as low as 10°F before milling did not increase or decrease breakage. Work is continuing in this area as well as on the effects of low temperature on hull removal. Microwave heating of rough rice to 185° and 210°F decreased the yield of head rice milled at room temperature from 69 percent to 60 and 43 percent, respectively.

Publications

NEW AND IMPROVED FOOD PRODUCTS

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